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Selective Hydrogenation of Benzene to Cyclohexene over Monometallic Ru Catalysts: Investigation of ZnO and ZnSO\textsubscript{4} as Reaction Additives as Well as Particle Size Effect

Haijie Sun \textsuperscript{1}, Zhihao Chen \textsuperscript{2,}*, Chenggang Li \textsuperscript{1}, Lingxia Chen \textsuperscript{1}, Yan Li \textsuperscript{1}, Zhikun Peng \textsuperscript{3,}*, Zhongyi Liu \textsuperscript{3} and Shouchang Liu \textsuperscript{3}

\textsuperscript{1} Institute of Environmental and Catalytic Engineering, College of Chemistry and Chemical Engineering, Zhengzhou Normal University, Zhengzhou 450044, China; sunhaijie406@zznu.edu.cn (H.S.); zznu_lcg@163.com (C.L.); clingxia@vip.163.com (L.C.); nanyangershier@163.com (Y.L.)

\textsuperscript{2} Zhengzhou Tobacco Research Institute of CNTC, Zhengzhou 450001, China

\textsuperscript{3} College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou 450001, China; liuzhongyi406@163.com (Z.L.); liushouchang406@163.com (S.L.)

* Correspondence: chenzh@ztri.com.cn (Z.C.); Zhikunpeng@163.com (Z.P.); Tel.: +86-371-6767-2762 (Z.C.)

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Abstract: Monometallic Ru catalysts with different particle size were prepared via a precipitation method and reduced at different temperatures. In addition, their catalytic activity towards cyclohexene formation from selective hydrogenation of benzene was investigated. With the utilization of ZnO and ZnSO\textsubscript{4} as reaction additives, (Zn(OH))\textsubscript{3}(ZnSO\textsubscript{4})(H\textsubscript{2}O)\textsubscript{3} could be generated and chemisorbed on the Ru surface, which played a crucial role on increasing the selectivity to cyclohexene and retarding the catalytic activity towards benzene conversion. Interestingly, without addition of ZnO and ZnSO\textsubscript{4}, no cyclohexene was observed over all tested Ru catalysts with different particle sizes. This suggested that particle size plays no role in cyclohexene synthesis from selective hydrogenation of benzene over the pure monometallic Ru catalysts in the absence of ZnO and ZnSO\textsubscript{4}. On the other hand, when both ZnO and ZnSO\textsubscript{4} were applied, surface n(Zn\textsuperscript{2+})/n(Ru) molar ratio increased with increasing particle size of the monometallic Ru catalysts after catalytic experiments, demonstrating that the content of chemisorbed (Zn(OH))\textsubscript{3}(ZnSO\textsubscript{4})(H\textsubscript{2}O)\textsubscript{3} on Ru catalysts surface is enhanced under such a circumstance. More importantly, the maximum cyclohexene yield obtained over monometallic Ru catalysts showed a volcanic-type variation with increasing particle size of Ru from 3.6 nm to 5.6 nm. When the particle size of the monometallic Ru catalyst was 4.7 nm, the highest cyclohexene yield of 60.4% was achieved with an optimum n(ZnO)/n(Ru) ratio of 0.19:1 in the presence of 0.62 mol-dm\textsuperscript{-3} ZnSO\textsubscript{4} within 25 min of catalytic experiments at 423 K under 5.0 MPa of H\textsubscript{2}. In addition, no decrease of catalytic activity towards cyclohexene generation was observed over this catalyst after 10 catalytic experiments without any regeneration.

Keywords: selective hydrogenation; cyclohexene; particle size; reaction additives

1. Introduction

Caprolactam and adipic acid are of great importance for the modern chemical industry, since they play significant roles in producing nylon 6, nylon 66, polyamide, polyester. Both are widely utilized in the textiles, transportation and electronic industries, among others. Therefore, the selective hydrogenation of benzene to cyclohexene has drawn great industrial and academic interest, because cyclohexene can be easily converted to caprolactam and adipic acid by typical olefin reactions.
which is safe, energy conserving, environmentally friendly and might result in high carbon atom economy [1–6]. On the other hand, cyclohexane, as the only side product from selective hydrogenation of benzene, can be utilized for production of caprolactam and adipic acid as well [7–10]. However, it is thermodynamically difficult to obtain cyclohexene, since the standard free energy change for cyclohexane formation from benzene hydrogenation is $-98 \text{kJ} \cdot \text{mol}^{-1}$, while that for cyclohexene formation is $-23 \text{kJ} \cdot \text{mol}^{-1}$ [11–14]. Therefore, deeper understanding for designing the catalytic system is a promising way to overcome this challenge.

In heterogeneous catalysis, the catalytic activity and selectivity of nanoparticles are often considered to be related to the particle size of catalysts. This is mainly attributed to the fact that their particle size controls the number of corner, edge, and face atoms on the catalyst surface, which are of great significance for the adsorption and activation of substrates [15–17]. Nagahara et al. [18] reported that catalytic activity towards benzene conversion to cyclohexene generation over Ru catalysts might be affected by the particle size of Ru. In addition, industrial validity was achieved using a 5 nm, unsupported Ru-Zn catalyst. However, the reason Ru particle size could influence the catalytic activity and selectivity to cyclohexene formation was not revealed. More importantly, up to now, this issue is still considered controversial. For instance, it was suggested by Milone et al. [19] that no particle size effect was observed for Ru-catalyzed selective hydrogenation of benzene to cyclohexene. They found that the selectivity to cyclohexene did not change when the particle size of Ru catalysts increased from 2 nm to 13 nm. This was attributed to fact that hydrogenation of benzene and cyclohexene take place on the same type of active sites. On the contrary, Bu et al. [20] reported that the maximum cyclohexene yield obtained over Ru catalysts showed a volcanic-type variation when increasing the particle size of Ru from 3.6 nm to 7.6 nm. The highest cyclohexene yield was achieved when the Ru particle size was 5.6 nm, and this was because there then exist the most active sites which are suitable for cyclohexene generation. Furthermore, it was also reported by Zhou et al. [2] that the catalytic activity towards benzene conversion increased with increasing Ru particle size from 2.4 nm to 5.4 nm. However, the selectivity towards cyclohexene exhibited a volcanic-type variation as well, and the highest initial cyclohexene selectivity was obtained over the Ru catalyst with particle size 4.4 nm. They deemed that the particle size could control the number of corner, edge, and face atoms on the catalyst surface, affecting the catalytic activity and selectivity towards cyclohexene synthesis. Based on the aforementioned results, it is, therefore, of great scientific and industrial interest to investigate how the particle size affects the cyclohexene formation form selective hydrogenation of benzene.

Additionally, it was demonstrated by Nagahara et al. [18] that Zn as a promoter could significantly improve the catalytic selectivity towards cyclohexene synthesis over Ru-Zn catalysts. Further, Sun et al. [21,22] reported that Zn exists as ZnO in unsupported Ru-Zn catalysts, and it could react with ZnSO$_4$ to generate a $(\text{Zn(OH)}_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_5$ salt, which plays a key role in improving the catalytic activity for the formation of cyclohexene. However, since Ru-Zn catalysts were prepared and utilized integrally, it is difficult to distinguish the roles that different Zn compounds (e.g., ZnO, ZnSO$_4$ and $(\text{Zn(OH)}_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_5$) play in increasing the selectivity to cyclohexene from partial hydrogenation of benzene.

Thus, in this work, the promotion effect of ZnO and ZnSO$_4$ as reaction additives was investigated over a simple monometallic Ru catalyst. More importantly, nano-scaled monometallic Ru catalysts with different particle size were prepared via precipitation method and reduced at different temperature, and the catalysts were evaluated for selective hydrogenation of benzene to cyclohexene to reveal the real mechanism of how the particle size of Ru affects the catalytic selectivity towards cyclohexene formation.

2. Results

2.1. Effects of ZnO and ZnSO$_4$

Figure 1a illustrates the XRD patterns of Ru-4.7 catalyst with addition of different content of ZnO in the presence of ZnSO$_4$ (0.62 mol·L$^{-1}$) after catalytic experiments. Characteristic diffractions
corresponding to metallic Ru were observed over all measured samples, demonstrating that Ru exists mainly as a metallic state (PDF: 01-0770-0247). Furthermore, when the molar ratio of ZnO to Ru rises to 0.17, the reflections related to (Zn(OH)$_2$)$_3$(ZnSO$_4$)(H$_2$O)$_3$ starts to be shown (PDF: 01-0780-0247). In addition, the intensity of its reflections enhances with increasing the molar ratio of ZnO to Ru from 0.17 to 0.34, indicating that (Zn(OH)$_2$)$_3$(ZnSO$_4$)(H$_2$O)$_3$ was generated during the catalytic experiments via the reaction between ZnO and ZnSO$_4$ and was then chemisorbed on the Ru surface. Moreover, the content of (Zn(OH)$_2$)$_3$(ZnSO$_4$)(H$_2$O)$_3$ increases with rising the molar ration of ZnO to Ru. On the other hand, Figure 1b shows the XRD patterns of Ru-4.7 catalyst after catalytic experiments with addition of only ZnO (n(ZnO)/n(Ru) = 0.19), only ZnSO$_4$ (0.62 mol·L$^{-1}$), both ZnO (n(ZnO)/n(Ru) = 0.19) and ZnSO$_4$ (0.62 mol·L$^{-1}$) or without any additives, respectively. Reflections attributed to metallic Ru were detected over all analyzed catalysts, revealing the existence of metallic Ru as well. In addition, characteristic diffractions of ZnO were observed when only ZnO was added as an additive (PDF:01-0770-2551), indicating that ZnO could not be reduced during the reaction. In comparison, (Zn(OH)$_2$)$_3$(ZnSO$_4$)(H$_2$O)$_3$ was only pronounced over Ru-4.7 after catalytic experiment with addition of both ZnO (n(ZnO)/n(Ru) = 0.19) and ZnSO$_4$ (0.62 mol·L$^{-1}$). These observations indicate that the presence of both ZnSO$_4$ and ZnO is crucial for the formation of (Zn(OH)$_2$)$_3$(ZnSO$_4$)(H$_2$O)$_3$.

**Figure 1.** XRD patterns of the Ru-4.7 catalyst with different additives after catalytic experiments. (a) by adding different content of ZnO in the presence of ZnSO$_4$ (0.62 mol·L$^{-1}$); (b) with addition of only ZnO (n(ZnO)/n(Ru) = 0.19), only ZnSO$_4$ (0.62 mol·L$^{-1}$), both ZnO (n(ZnO)/n(Ru) = 0.19) and ZnSO$_4$ (0.62 mol·L$^{-1}$) or without any additives.

H$_2$-TPR profile of a non-reduced Ru sample is shown in Figure 2. A reduction peak with a small shoulder peak can be observed at a range between 300–520 K, which is corresponding to the reduction of Ru$^{3+}$→Ru$^{2+}$→Ru$^{0}$ [23]. In addition, the hydrogen consumption of 11.9 µmol H$_2$/mg catalyst is obtained from a standard CuO calibration, which gives 80.2% of Ru content. This is consistent with that obtained from AAS (e.g., 80.4%). These results indicate that Ru could be completely reduced via the reduction procedure and exist as metallic state through the whole time, which are consistent to the XRD results.
Table 1 shows the concentration of ZnSO$_4$ ($c_{\text{ZnSO}_4}$), molar ratio of Zn to Ru as well as S to Ru, particle size of the Ru-4.7 catalyst and pH values of the slurry after catalytic experiments. Neither Zn nor S species can be detected after reaction without any additives (1st row). By adding only ZnSO$_4$ as an additive, slight amount of Zn (e.g., $n(\text{Zn})/n(\text{Ru}) = 0.0313$) and S (e.g., $n(\text{S})/n(\text{Ru}) = 0.0026$) was observed after hydrogenation (2nd row). It was reported by Sun et al. [24] that slender quantities of $(\text{Zn(OH)}_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_3$ can be generated via the hydrolysis of ZnSO$_4$. The same situation can be applied in this case. Furthermore, with only addition of ZnO, only Zn was detected after catalytic experiment (9th row). When both ZnSO$_4$ and ZnO are utilized as additives, the molar ratio of Zn to Ru as well as S to Ru increase with increasing the ZnO content after catalytic experiments, enlightening the enhancement of the chemisorbed $(\text{Zn(OH)}_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_3$ on the Ru surface. This is consistent with the XRD results. It is worth noting that the particle size of Ru after reaction with all measured samples are comparable, i.e., $\approx 4.7$ nm, indicating that the particle size of Ru does not change very much during the reaction. Additionally, the pH value of the slurry considerably decreases after the catalytic experiments with the presence of ZnSO$_4$ (e.g., 5.53 of pH value with only addition of ZnSO$_4$ vs. 7.10 of pH value with only addition of ZnO). This can be rationalized in terms of the hydrolysis of ZnSO$_4$, resulting in the acidic environment. The pH value of the slurry continuously increases when raising the ZnO content, which is because ZnO can react with ZnSO$_4$ to form the $(\text{Zn(OH)}_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_3$ salt. The concentration of ZnSO$_4$ decreases, hence the pH value rises.

Figure 3 demonstrates the TEM images of the Ru-4.7 catalysts for selective hydrogenation of benzene to cyclohexene with different additives (Figure 3a–d), and the SEM image as well as the Element mapping image of Ru-4.7 catalyst in the presence of both ZnO and ZnSO$_4$ after catalytic experiments.
experiments (Figure 3e,f). As can be seen, Ru particles over all analyzed samples display a circular or elliptical shape after reaction. In addition, the particle size of Ru is around 5 nm, which is in good agreement with XRD results (Figure 3a–d). Moreover, the stick shape of ZnO was observed when only ZnO was added as an additive (Figure 3b), suggesting that ZnO can be hardly dispersed on the Ru surface. In addition, it can be observed from Figure 3e,f that Zn and S species homogeneously dispersed on the Ru surface of Ru-4.7 AH. This indicates that the generated \((\text{Zn(OH)}_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_3\) salt is uniformly dispersed on the Ru surface as well.

![Figure 3](image1)

**Figure 3.** TEM images of the Ru-4.7 catalysts for selective hydrogenation of benzene to cyclohexene with different additives after catalytic experiments. (a) Blank; (b) ZnO; (c) ZnSO4; (d) ZnO and ZnSO4; (e) SEM image and (f) element mapping image of Ru-4.7 catalyst after catalytic experiments in the presence of both ZnO and ZnSO4.

The wettability of Ru catalyst surface was further investigated both in the absence and in the presence of ZnO and ZnSO4. Water droplets on pure Ru as well as Ru with ZnO and ZnSO4 are shown in Figure 4. As demonstrated, when ZnO and ZnSO4 were utilized as reaction additives, the contact angle significantly decreased in comparison to that observed from Ru without adding ZnO and ZnSO4. This suggests that hydrophilicity of Ru surface was highly improved by the chemisorbed \((\text{Zn(OH)}_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_3\) salt.

![Figure 4](image2)

**Figure 4.** Water contact angle of Ru catalysts after catalytic experiments. (a) Ru without any additives; (b) Ru with ZnO and ZnSO4 as reaction additives.
XPS spectra of the Ru catalyst with a particle size of 4.7 nm before and after catalytic experiments were demonstrated in Figure 5. Figure 5a gives a peak at 461.2 eV that is attributed to Ru 3p3/2. This shows that Ru exists in a metallic state [25], which is consistent with XRD results. As can be observed from Figure 5b, the electron-binding energy of Ru 3p3/2 over Ru-4.7 AH is 462.5 eV, indicating the existence of metallic Ru as well [26]. It is worth noting that, since the electron-binding energy of Ru-4.7 AH is 1.3 eV higher than that observed over Ru-4.7, it can be concluded that Ru5+ species of electron deficiency is generated during the catalytic experiment. Additionally, the deconvoluted electron-binding energy of Zn 2p2/3 and the Auger electron kinetic energy of Zn-LMM was observed at 1022.0 eV and 988.6 eV over Ru-4.7 AH, respectively (Figure 5c,d), suggesting that Zn species mainly exist as Zn2+ after reaction [27,28]. In addition, it is observed that the electron-binding energy of Zn 2p2/3 (1022.0 eV) is lower than that obtained over Zn(OH)2 (1022.7 eV) [29] as well as ZnSO4 (1023.0 eV) [30]. This implies that the lost electrons were transferred from Ru to Zn2+. Furthermore, Figure 5e shows that the electron-binding energy of S 2p is 169.6 eV, indicating that S species mainly exist as SO42− [31]. Struijk et al. [32] also found that the electron-binding energy of S 2p on the surface of Ru catalyst after hydrogenation in ZnSO4 was 169.9 eV, and S species were in the form of SO42−.

![Figure 5](image-url)

**Figure 5.** XPS spectra of the Ru catalyst with a particle size of 4.7 nm before and after catalytic experiments. (a) binding energy of Ru 3p3/2 for Ru-4.7 catalyst; (b) binding energy of Ru 3p3/2 for Ru-4.7 AH; (c) binding energy of Zn 2p3/2 for Ru-4.7 AH; (d) Auger electron kinetic energy of Zn LMM for Ru-4.7 AH; (e) binding energy of S 2p for Ru-4.7 AH.

Figure 6 exhibits the catalytic activity towards cyclohexene formation from selective hydrogenation of benzene over Ru-4.7 catalyst with the different molar ratio of ZnO to Ru in the presence of ZnSO4. It is obvious that the catalytic activity towards benzene conversion declines when increasing the added ZnO content. Meanwhile, in contrast, the selectivity towards cyclohexene formation grows. In addition, cyclohexene yield of 60.4% was obtained when the molar ratio of ZnO to Ru is 0.19, which is one of the highest yields of cyclohexene reported by far [33–35]. Furthermore, as can
be observed in Figure 7, no cyclohexene was detected without any additives. In comparison, 2.1% and 33% of cyclohexene yield was achieved when only ZnO or only ZnSO$_4$ was added, respectively.

**Figure 6.** Catalytic activity towards cyclohexene formation from selective hydrogenation of benzene over Ru-4.7 catalyst with the different molar ratio of ZnO to Ru in the presence of ZnSO$_4$ ($m_{\text{cat}} = 2.0$ g, $m_{\text{ZnSO}_4} = 50.0$ g, $v_{\text{H}_2} = 280$ mL, $v_{\text{benzene}} = 140$ mL, $T = 423$ K, $p_{\text{H}_2} = 5.0$ MPa). (a) catalytic activity towards benzene conversion over Ru-4.7 catalyst, (b) catalytic selectivity towards cyclohexene formation and (c) yield of cyclohexene over Ru-4.7 catalyst with the different molar ratio of ZnO to Ru in the presence of ZnSO$_4$.

**Figure 7.** Catalytic activity towards cyclohexene formation from selective hydrogenation of benzene over Ru-4.7 catalyst with different additives ($m_{\text{cat}} = 2.0$ g, $v_{\text{H}_2} = 280$ mL, $v_{\text{benzene}} = 140$ mL, $T = 423$ K, $p_{\text{H}_2} = 5.0$ MPa). (a) Catalytic activity towards benzene conversion, (b) catalytic selectivity towards cyclohexene formation and (c) yield of cyclohexene over Ru-4.7 catalyst with different additives.

Combined with catalytic experimental results as well as the characterization outcomes, it can be concluded that the chemisorbed $(\text{Zn(OH)}_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_3$ salt plays a key role in the synthesis of cyclohexene from selective hydrogenation of benzene. The significance of $(\text{Zn(OH)}_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_3$ salt can be ascribed as follows: (1) Zn$^{2+}$ of the chemisorbed $(\text{Zn(OH)}_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_3$ salt on the Ru surface could transfer the electrons from Ru to Zn, which leads to generating the Ru$^{3+}$ species of electron deficiency. It has been reported that the generated Ru$^{3+}$ species of electron deficiency has a weaker ability to absorb cyclohexene, resulting in the faster desorption of the formed cyclohexene to avoid the further hydrogenation of cyclohexene [36]; (2) A stable complex could be formed between Zn$^{2+}$ of the chemisorbed $(\text{Zn(OH)}_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_3$ salt on the Ru surface and cyclohexene via hydrogen bonds, achieving the similar effect of the electron modification to increase the selectivity to cyclohexene [37]; (3) Zn$^{2+}$ of the chemisorbed $(\text{Zn(OH)}_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_3$ salt might selectively cover some strong active sites of Ru which are not suitable for the synthesis of cyclohexene, thus
more benzene and cyclohexene could be adsorbed on the weaker active sites. These bring about the increase of selectivity to cyclohexene as well as the decline of the catalytic activity towards benzene conversion [32]; (4) Hydrophilicity of Ru surface could be significantly improved by the chemisorbed (Zn(OH)2)3(ZnSO4)(H2O)3 salt, resulting in the formation of a stagnant water layer. Since the solubility of cyclohexene is much lower than that of benzene, desorption of cyclohexene from the catalyst surface would be obviously increased [32]. Therefore, a decrease of the benzene conversion as well as an increase of cyclohexene selectivity were observed when a higher amount of the (Zn(OH)2)3(ZnSO4)(H2O)3 salt was adsorbed on the Ru surface. Based on the observations, a plausible sketch of surface structure of Ru-4.7 catalysts with the different additives was demonstrated in Figure 8. Without any additives (Figure 8A), no Zn2+ was chemisorbed on the Ru surface, resulting in the complete hydrogenation of benzene to cyclohexane. By applying ZnO as an additive (Figure 8B), the adsorbed Zn was mainly stick shape of ZnO which cannot be dispersed on the Ru surface and no electrons could be transferred from Ru to Zn. Only 2.1% of maximum cyclohexene was, hence, obtained when only ZnO was added. However, when ZnSO4 was utilized as the unique additive, a small quantity of (Zn(OH)2)3(ZnSO4)(H2O)3 salt was generated due to the hydrolysis of ZnSO4 under the reaction condition (Figure 8C). In addition, the (Zn(OH)2)3(ZnSO4)(H2O)3 salt could be chemisorbed and dispersed on the Ru surface, leading to a 33% of maximum cyclohexene yield. In addition, the amount of the chemisorbed (Zn(OH)2)3(ZnSO4)(H2O)3 salt rises when increasing the ZnO content when both ZnO and ZnSO4 are present (Figure 8D). Notably, even (Zn(OH)2)3(ZnSO4)(H2O)3 salt is the essence of the synthesis of cyclohexene, and there is an optimum content for that since the enhancement of the cyclohexene selectivity is accompanied by the drop of the catalytic activity towards benzene conversion. Therefore, the highest yield of cyclohexene (60.4%) was achieved when the molar ratio of ZnO to Ru reached 0.19.

![Figure 8](image_url)

**Figure 8.** Sketch of surface structure of Ru-4.7 catalysts with the different additives. (A) surface structure of Ru-4.7 without any additives; (B) surface structure of Ru-4.7 with only ZnO as a reaction additive; (C) surface structure of Ru-4.7 with only ZnSO4 as a reaction additive; (D) surface structure of Ru-4.7 with both ZnO and ZnSO4 as reaction additives.

### 2.2. Effects of Particle Size of Ru Catalysts

Monometallic Ru catalysts with different particle size before and after catalytic experiments were analyzed by XRD (Figure 9a,b). As can be seen from Figure 9a, characteristic diffractions...
related to metallic Ru were observed over all measured samples, indicating that Ru exists mainly in a metallic state. Additionally, the particle size of Ru from top to bottom was calculated to be 5.6, 4.7, 4.1 and 3.5 nm via Scherrer equation, respectively. Furthermore, the intensity of diffractions at 44° decreases from top to bottom, indicating the decline of the particle size as well. On the other hand, Figure 9b exhibits the XRD patterns of Ru catalysts with different particle size after the reaction. As can be observed, characteristic diffractions related to metallic Ru were also shown over all samples, revealing that Ru exists in a metallic state as well after catalytic experiments. In addition, the particle size of Ru from top to bottom was calculated to be 5.9, 4.7, 4.2 and 3.6 nm respectively, according to the Scherrer equation. These demonstrated that the Ru particle size did not change very much during the reaction process. However, several new diffractions were noticed in Figure 9b, which correspond to (Zn(OH)$_2$)$_3$(ZnSO$_4$)(H$_2$O)$_3$ salt. This can be rationalized by observing that (Zn(OH)$_2$)$_3$(ZnSO$_4$)(H$_2$O)$_3$ was generated from the reaction between ZnO and ZnSO$_4$ and was then chemisorbed on the Ru catalysts surface. In addition, it was also displayed that the intensity of (Zn(OH)$_2$)$_3$(ZnSO$_4$)(H$_2$O)$_3$ gradually increased with increasing particle size of Ru catalysts, demonstrating that (Zn(OH)$_2$)$_3$(ZnSO$_4$)(H$_2$O)$_3$ started to accumulate on the catalysts surface when Ru particle size increased from 3.5 to 5.6 nm.

![Figure 9. XRD patterns of Ru catalysts with the different particle size before (a) and after (b) catalytic experiments.](image)

Figure 10 gives the HTEM images, EDS, and particle size distribution of the Ru catalysts with the different particle sizes after catalytic experiments. All Ru catalysts display circular or elliptical shape. Furthermore, particle size of Ru-3.5 AH, Ru-4.1 AH, Ru-4.7 AH and Ru-5.6 AH is mainly distributed at 3.4, 4.0, 4.9 and 5.4 nm, respectively, which is consistent with the results obtained from XRD. In addition, as can be seen from the EDS results, the molar ration of Zn to Ru on the catalysts surface increased from 0.3 (1.44/44.46) over Ru-3.5 AH to 0.7 (3.23/47.02) over Ru-3.5 AH. This is attributed to the fact that (Zn(OH)$_2$)$_3$(ZnSO$_4$)(H$_2$O)$_3$ salt starts to accumulate, which is in a good agreement with XRD results.

Textural properties of the Ru catalysts with different particle sizes before and after catalytic experiments are listed in Table 2. Decrease of the specific surface area and pore volume as well as an increase of pore diameter was observed with increasing particle size of Ru catalysts for both before and after catalytic experiments. Moreover, it is noticed that the specific surface area (e.g., 70 m$^2$ g$^{-1}$ over Ru-3.5 AH) and the pore volume (e.g., 0.15 cm$^3$ g$^{-1}$ over Ru-3.5 AH) after reaction is lower in comparison to that obtained over fresh catalysts (e.g., 78 m$^2$ g$^{-1}$ of specific surface area and 0.17 cm$^3$ g$^{-1}$ of pore volume over Ru-3.5). The pore diameter after catalytic experiments, however, is higher than that observed before catalytic experiments (e.g., 6.16 nm over Ru-3.5 AH vs. 5.48 nm over Ru-3.5). This might be because parts of the pores were blocked by the chemisorbed (Zn(OH)$_2$)$_3$(ZnSO$_4$)(H$_2$O)$_3$ salt.
The catalytic activity towards benzene conversion and selectivity for cyclohexene formation over Ru catalysts with different particle size in the presence of ZnO and ZnSO\textsubscript{4} was demonstrated in Figure 11a–c. An obvious increase of catalytic activity towards benzene conversion as well as a decrease of cyclohexene selectivity was observed with increasing the particle size of Ru catalysts from 3.5 nm to 5.6 nm. Furthermore, the maximum yield (Max\textsubscript{yield}) of cyclohexene achieved over Ru catalysts with different particle size was displayed in Figure 11d. It can be seen that the highest maximum yield of cyclohexene of 60.4% was given over Ru-4.7 catalyst, and the maximum cyclohexene yield obtained over Ru catalysts shows a volcanic-type variation when increasing the particle size of Ru from 3.6 to 5.6 nm. Therefore, in this work, it can be concluded that there is an obvious particle size effect for the catalytic selective hydrogenation of benzene to cyclohexene over the Ru catalysts in the presence of ZnO and ZnSO\textsubscript{4}. Similar results were reported by Bu et al. [20] and Sun et al. [38] over Ru-Ba catalysts and Ru-Zn catalysts, respectively.

**Figure 10.** HRTEM images, EDS, and particle size distribution of the Ru catalysts with the different particle size after hydrogenation. First row (a–c), second row (d–f), third row (g–i) and last row (j–l) belongs to Ru-3.5 AH, Ru-4.1 AH, Ru-4.7 AH and Ru-5.6 AH, respectively.
Table 2. Textural properties of the Ru catalysts with the different particle size before and after catalytic experiments, including specific surface area ($S_{\text{BET}}$), pore volume ($V_p$) and pore diameter ($d_p$).

| Catalyst | $S_{\text{BET}}$/m$^2$ g$^{-1}$ | $V_p$/cm$^3$ g$^{-1}$ | $d_p$/nm |
|----------|--------------------------------|------------------------|-----------|
| Ru-3.5   | 78                             | 0.17                   | 5.48      |
| Ru-4.1   | 75                             | 0.15                   | 7.54      |
| Ru-4.7   | 69                             | 0.13                   | 8.60      |
| Ru-5.6   | 68                             | 0.11                   | 9.48      |
| Ru-3.5 AH| 70                             | 0.15                   | 6.16      |
| Ru-4.1 AH| 68                             | 0.13                   | 8.26      |
| Ru-4.7 AH| 65                             | 0.11                   | 8.88      |
| Ru-5.6 AH| 62                             | 0.10                   | 10.08     |

Figure 11. Benzene conversion (a) and cyclohexene yield (c) as function of time as well as cyclohexene selectivity (b) as function of benzene conversion and the maximum cyclohexene yield (d) over Ru catalyst with the different particle size ($m_{\text{cat}} = 2.0$ g, $m_{\text{ZnO}} = 0.3$ g, $m_{\text{ZnSO}_4} = 50.0$ g, $v_{\text{H}_2\text{O}} = 280$ mL, $v_{\text{benzene}} = 140$ mL, $T = 423$ K, $P_{\text{H}_2} = 5.0$ MPa).

The reaction course of selective hydrogenation of benzene over the Ru-4.7 catalyst under the optimized condition is illustrated in Figure 12. As can be observed, the yield of cyclohexene increased in the first 25 min and the highest cyclohexene yield of 60.4% was achieved at 25 min. Then the yield of cyclohexene starts to decrease while cyclohexane yield keeps increasing during the whole reaction, suggesting that hydrogenation of benzene is a typical continuous reaction. However, it is worth mentioning that the rate of cyclohexene yield declining is rather slow (49.5% of cyclohexene yield was obtained when 98.1% of benzene conversion was observed at 60 min), indicating that the further hydrogenation of cyclohexene to cyclohexane is effectively retarded.

To obtain a deeper understanding of the mechanism regarding how the particle size of Ru affects the cyclohexene formation, Ru-3.5 AH, Ru-4.1 AH, Ru-4.7 AH and Ru-5.6 AH were tested for selective hydrogenation of benzene to cyclohexene without utilizing ZnO and ZnSO$_4$·7H$_2$O as well (Figure 13). Complete conversion of benzene towards cyclohexane generation was observed over all tested Ru catalysts (2 g) within 5 min of reaction time, and no cyclohexene was detected. Furthermore, the hydrogenation of benzene was conducted over 1 g of the catalysts. Although the decline of the
catalytic activity towards benzene conversion emerged, cyclohexene was still not detected. This demonstrates that there is no particle size effect of the Ru catalyst for selective hydrogenation of benzene to cyclohexene without any additives, which is confirmed by Milone et al. as well [19]. Therefore, based on aforementioned observations, how the particle size of Ru catalysts affects the catalytic activity towards cyclohexene formation can be deemed as a result of the following two reasons: firstly, the content of $(\text{Zn(OH)}_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_3$ on the Ru catalysts surface increased with increasing the particle size of Ru, leading to a raise of the surface Zn/Ru molar ratio. This results in more electrons being transferred from Ru to Zn$^{2+}$, then more Ru$^{5+}$ species of electron deficiency being generated during the catalytic experiments. It has been reported that Ru$^{5+}$ species of electron deficiency could enhance the desorption of cyclohexene from Ru catalysts surface to retard the further hydrogenation of cyclohexane to cyclohexene, resulting in an increase of the selectivity to cyclohexene [36]. Another reason is that the pore width increases when raising the particle size of Ru catalysts, benefitting the desorption of cyclohexene from the pores of Ru catalysts. This could drastically suppress the further hydrogenation of cyclohexane to cyclohexene [39]. However, a decrease of catalytic activity towards benzene conversion was observed when increasing the particle size of Ru catalysts as well as the selectivity to cyclohexene. Thus, the highest cyclohexene yield was obtained over Ru-4.7 with considerably high benzene conversion (78.3%) and selectivity to cyclohexene (77.1%) after 25 min of reaction time.

**Figure 12.** Reaction course of benzene hydrogenation over the Ru-4.7 catalyst under the optimized condition ($m_{\text{cat}} = 2.0$ g, $m_{\text{ZnO}} = 0.3$ g, $m_{\text{ZnSO}_4} = 50.0$ g, $v_{\text{H}_2\text{O}} = 280$ mL, $v_{\text{benzene}} = 140$ mL, $T = 423$ K, $p_{\text{H}_2} = 5.0$ MPa).

**Figure 13.** Catalytic activity towards benzene conversion over Ru catalysts with the different particle size for hydrogenation of benzene without any additives ($v_{\text{H}_2\text{O}} = 280$ mL, $v_{\text{benzene}} = 140$ mL, $T = 423$ K, $p_{\text{H}_2} = 5.0$ MPa).
2.3. Reusability of Ru-4.7 Catalyst

The reusability of Ru-4.7 catalyst was tested under the same reaction conditions without further regeneration (Figure 14). No obvious deactivation was found after 10 catalytic experiments, and the Ru-4.7 catalyst gives at least 76.8% of benzene conversion and 75.4% selectivity to cyclohexene. The maximum yield of cyclohexene remains above 59.6% after 25 min of reaction time. This indicates that the Ru-4.7 catalyst possesses a great potential for industrial application on selective hydrogenation of benzene towards cyclohexene production.

![Figure 14. Catalytic activity towards benzene conversion, selectivity to cyclohexene and maximum yield of cyclohexene over Ru-4.7 catalyst for 10 runs of catalytic experiments (vH2O = 280 mL, vbenzene = 140 mL, T = 423 K, pH2 = 5.0 MPa).](image)

3. Materials and Methods

3.1. Chemicals

RuCl3·3H2O was commercially obtained from Sino-Platinum Co. Ltd. (Kunming, China). ZnSO4·7H2O was purchased from Fuchen Chemical Reagent Factory (Tianjin, China). NaOH and benzene were delivered from Kemiu Chemical Reagent Co. Ltd. (Tianjin, China). ZnO was bought from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All chemicals were of analytical grade without further purification and distilled water was applied in all experiments.

3.2. Preparation of Catalysts

Monometallic Ru catalysts were prepared as follows: 10.0 g RuCl3·3H2O precursor was dissolved in 200 cm³ of distilled water. Then 200 cm³ of 5 wt % NaOH aqueous solution was added at 353 K with continuous stirring for 2 h, followed by a reduction procedure in a 1000 cm³ Hastelloy autoclave under 5.0 MPa of H2 and a stirring speed of 800 min⁻¹ at 373 K, 393 K, 413 K and 433 K for 5 h, respectively. Neither drying nor calcination procedure were conducted before the reduction of catalysts. In addition, it should be noticed that the particle size of Ru catalysts was obtained via X-ray diffraction method, which was calculated to be 3.5 nm, 4.1 nm, 4.7 nm and 5.6 nm, respectively. To be clarified, the Ru catalysts synthesized at different reduction temperature were denoted as Ru-3.5, Ru-4.1, Ru-4.7 and Ru-5.6, respectively.

3.3. Catalytic Experimental Procedure

All catalytic experiments were carried out in a GS-1 type Hastelloy autoclave of 1000 cm³. In a typical selective hydrogenation of benzene to cyclohexene reaction, 2.0 g monometallic Ru catalyst, 50.0 g ZnSO4·7H2O as well as 280 cm³ distilled water were added in the autoclave. Then the reactor was heated up to 423 K under 5.0 MPa of H2 with a stirring speed of 800 min⁻¹ at 373 K, 393 K, 413 K and 433 K for 5 h, respectively. To be clarified, the Ru catalysts synthesized at different reduction temperature were denoted as Ru-3.5, Ru-4.1, Ru-4.7 and Ru-5.6, respectively.
was purified using \( \text{N}_2 \) for 4 times and followed by purification with \( \text{H}_2 \) for another 4 times as well. After that, the reactor was heated up to 423 K under 5.0 MPa of \( \text{H}_2 \) with a stirring speed of 800 min\(^{-1}\), followed by adding 140 cm\(^3\) benzene and adjusting the stirring speed to 1400 min\(^{-1}\) to eliminate the mass transfer limitation [18]. Subsequently, the liquid samples were taken periodically from the reactor every 5 min. All withdrawn samples were analyzed by gas chromatography from Hangzhou Kexiao Chemical Instrument and Equipment Co. Ltd. (Hangzhou, China) equipped with a flame ionization detector (FID). It is worth mentioning that all reagents and products (e.g., benzene, cyclohexene and cyclohexane) were calibrated, and correlation coefficient \((R^2)\) of all compounds is no less than 0.99.

In addition, the benzene conversion and selectivity towards cyclohexene were calculated with the obtained peak area with the area normalization method. After each reaction, the organic phase was removed via a separating funnel and the solid Ru catalyst together with the aqueous solution were added in the autoclave again in order to investigate the reusability of the catalysts via aforementioned experimental procedure. The Ru-3.5, Ru-4.1, Ru-4.7 and Ru-5.6 catalysts after hydrogenation reaction were denoted as Ru-3.5 AH, Ru-4.1 AH, Ru-4.7 AH and Ru-5.6 AH, respectively. To avoid \( \text{Zn}^{2+} \) impacting the characterization results, catalysts after the reaction were filtered and washed until the filtrate become neutralization and no \( \text{Zn}^{2+} \) was detected. Then solid samples were dried in Ar flow at 373 K and stored in the ethanol for further characterization.

### 3.4. Catalysts Characterization

X-ray diffraction (XRD) patterns for the fresh and spent catalysts were recorded at room temperature using an X’Pert Pro instrument from Philips (Almelo, The Netherlands). The diffracted intensity of Cu-K\(\alpha\) radiation \((\lambda = 0.154 \text{ nm})\) was measured at the range of 2\(\theta\) between 5\(^\circ\) and 90\(^\circ\), with a step size of 0.03\(^\circ\). Non-reduced solid Ru samples were pretreated under Ar atmosphere at 373 K for 6 h, which was further used for Ru content analysis and reducibility degree analysis, respectively. The Ru content was obtained by atomic absorption spectrometer (AAS) using a Perkin Elmer AAnalyst 300 from America (PerkinElmer, Waltham, MA, USA). In addition, temperature programmed reduction (TPR) was conducted with an Autosorb-IQ from Quantachrome (Boynton Beach, FL, USA). Typically, 10 mg of dried sample was firstly treated under an Ar flow for 2 h at room temperature. Then an Ar stream containing 10 Vol \% \( \text{H}_2 \) was introduced instead \((30 \text{ cm}^3 \text{ min}^{-1})\) while being heated till 573 K \((10 \text{ K min}^{-1})\) and held for 1 h. The hydrogen consumption was recorded and determined by using a standard CuO calibration. In addition, elemental analysis was obtained via X ray Fluorescence (XRF) using a S4 Pioneer instrument from Bruker AXS (Karlsruhe, Germany). Moreover, the valence state of Ru and Zn on the catalyst surface was analyzed by X-ray photoelectron spectroscopy (XPS) using a PHI Quantera SXM instrument from Ulvac-Phi (Chigasaki, Japan). Al K\(\alpha \) \((E_b = 1486.6 \text{ eV})\) was chosen as the source of radiation and vacuum degree was adjusted to be \(6.7 \times 10^{-8} \text{ Pa}\). The energy scale was calibrated and corrected for charging using the C1s \((E_b = 284.8 \text{ eV})\) line as the binding energy reference. The sample in the ethanol was supersonically pretreated for 30 min and dried in Ar. Then the powder was placed on the conducting resin for SEM analysis. The catalyst surface element scanning was tested by a SUMIGMA scanning electron microscope (SEM) from Carl Zeiss AG (Jena, Germany). The sample in the ethanol was pretreated using supersonic for 30 min as well, and then placed on a Cu board for TEM analysis. Furthermore, JEOL JEM 2100 transmission electron microscope (TEM) combined with energy dispersive spectrometer (EDS) was utilized to identify the surface composition of the selected samples. Textural properties were analyzed by the Nova 1000 e-Physisorption Analyzer (Boynton Beach, FL, USA). All the samples were evacuated at 523 K under the vacuum pressure for 2 h prior to the measurements and the isotherms were taken at 77 K. The specific surface area \((S_{\text{BET}})\) was determined by the Brunauer-Emmett-Teller (BET) model. To investigate the wettability of the catalyst surface, water contact angle values \((\text{CAs})\) were measured by a contact angle meter (JC2000 C1, Powereach, Shanghai, China) at ambient temperature for each sample.
4. Conclusions

(Zn(OH)$_2$)$_3$(ZnSO$_4$)(H$_2$O)$_3$ could be generated from ZnO and ZnSO$_4$ during catalytic experiments, which was then chemisorbed and uniformly dispersed on the surface of Ru-4.7 catalyst. It was demonstrated that the chemisorbed (Zn(OH)$_2$)$_3$(ZnSO$_4$)(H$_2$O)$_3$ plays the crucial role on improving the catalytic activity towards cyclohexene synthesis over Ru-4.7 catalyst, i.e., 60.4% of cyclohexene yield was obtained over Ru-4.7 catalyst when applying ZnO and ZnSO$_4$ as additives in comparison to that achieved over Ru-4.7 catalyst when only utilizing ZnO (2.1%) or ZnSO$_4$ (33.0%). More importantly, without adding ZnO and ZnSO$_4$, complete conversion of benzene was observed within 5 min and no cyclohexene was detected over all tested Ru catalysts with different particle sizes. This suggested that there is no particle size effect on cyclohexene synthesis from selective hydrogenation of benzene over the pure monometallic Ru catalysts in the absence of ZnO and ZnSO$_4$. On the other hand, when both ZnO and ZnSO$_4$ were utilized as the reaction additives, surface Zn$^{2+}$/Ru molar ratio increased with increasing the particle size of the monometallic Ru catalysts after catalytic experiments, indicating that the content of chemisorbed (Zn(OH)$_2$)$_3$(ZnSO$_4$)(H$_2$O)$_3$ on Ru catalysts raised under such a circumstance, which was confirmed from XRD results as well. In addition, the maximum cyclohexene yield obtained over monometallic Ru catalysts showed a volcanic-type variation when increasing the particle size of Ru from 3.6 to 5.6 nm. Therefore, the generation of (Zn(OH)$_2$)$_3$(ZnSO$_4$)(H$_2$O)$_3$ during the catalytic experiment was considered as the essence of the particle size effect over Ru catalysts on the selective hydrogenation of benzene to cyclohexene. The highest cyclohexene yield of 60.4% was achieved over Ru-4.7 with an optimum ZnO/Ru ratio of 0.19:1 in the presence of 0.62 mol·L$^{-1}$ ZnSO$_4$ within 25 min of catalytic experiment at 423 K under 5.0 MPa of H$_2$. In addition, no decrease of catalytic activity towards cyclohexene generation was observed over this catalyst after 10 catalytic experiments without any regeneration.

Author Contributions: Haijie Sun, Zhihao Chen and Zhikun Peng conceived and designed the experiments; Chenggang Li and Yan Li performed the experiments; Zhongyi Liu and Shouchang Liu analyzed the data; Lingxia Chen contributed reagents/materials/analysis tools; Haijie Sun wrote the paper.

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