

## Article

# Origin of the Increase in the Selectivity of Ru Catalysts with the Addition of Amines in the Presence of ZnSO<sub>4</sub> for the Selective Hydrogenation of Benzene to Cyclohexene

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**Abstract:** The synthesis of nylon 6 and nylon 66 can be performed, starting with the selective hydrogenation of benzene to cyclohexene, which is deemed to be environmentally friendly and cost-saving and to have higher atom efficiency. Nano-Ru catalyst was synthesized via a precipitation method. The prepared catalyst was evaluated in the selective hydrogenation of benzene toward cyclohexene generation in the presence of ZnSO<sub>4</sub> in a liquid batch reactor. The promotion effect of the addition of amines, i.e., ethylenediamine, ethanolamine, diethanolamine, and triethanolamine, was investigated. The fresh and spent catalysts were thoroughly characterized by XRD, TEM, AES, N<sub>2</sub>-sorption, FT-IR, and TPR. It was found that the addition of amines could significantly improve the catalytic selectivity toward cyclohexene formation in the presence of ZnSO<sub>4</sub>. This was attributed to the formation of (Zn(OH)<sub>2</sub>)<sub>5</sub>(ZnSO<sub>4</sub>)(H<sub>2</sub>O)<sub>x</sub> (x = 0.5, 3 or 4) through the reaction between ZnSO<sub>4</sub> and the amines, which could be chemisorbed on the Ru surface. This led to retarding the formation of cyclohexane from the complete hydrogenation of benzene and, thus, increased the catalytic selectivity toward cyclohexene synthesis. Therefore, with the presence of ZnSO<sub>4</sub>, the amount of chemisorbed (Zn(OH)<sub>2</sub>)<sub>5</sub>(ZnSO<sub>4</sub>)(H<sub>2</sub>O)<sub>x</sub> increased with increasing amounts of added amines, leading to a decline in the catalytic activity toward benzene conversion and selectivity toward cyclohexene generation. When 7.6 mmol of diethanolamine and 10 g of ZrO<sub>2</sub> were applied, the highest cyclohexene yields of 61.6% and 77.0% of benzene conversion were achieved over the Ru catalyst. Promising stability was demonstrated after six runs of catalytic experiments without regeneration. These achievements are not only promising for industrial application but also beneficial for designing other catalytic systems for selective hydrogenation.

**Keywords:** selective hydrogenation of benzene; cyclohexene; amines; Ru; ZnSO<sub>4</sub>



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## 1. Introduction

Cyclohexene, with an unstable double bond, is one of the most important intermediates in the chemical industry, and it can be utilized to synthesize adipic acid, nylon 6, nylon 66, etc. In comparison to some traditional methods, e.g., the dehydration of cyclohexanol, the dehydrochlorination of halogenated cyclohexane, and the dehydrogenation of cyclohexane, the selective hydrogenation of benzene toward cyclohexene production is deemed to be environmentally friendly, cost-saving, and to have higher atom efficiency [1–4]. Therefore, more and more attention is being given to cyclohexene generation through the selective hydrogenation of benzene.

Introducing organic additives [5–9] and inorganic additives [10–12] in the slurry is one of the most effective approaches to improve the yield of cyclohexene from the hydrogenation of benzene. It was reported by Struijk et al. [8] that the cyclohexene yield could be increased from 2% to 8% over the Ru catalyst with the addition of methanol to

the slurry. It was explained that the hydrogen bond formed between cyclohexene and the additive could decrease the adsorption enthalpy of cyclohexene on the Ru surface. This could improve the desorption rate of cyclohexene from the Ru surface and, thus, increase its yield. Furthermore, Spinacé et al. [9] found that some hydrated organic molecules could increase the hydrophilicity of Ru particles, which benefits the desorption of cyclohexene. It was reported that a 19% yield of cyclohexene was obtained over the Ru catalyst in ethylene glycol/water. It is worth noting that by applying organic additives only, a yield no higher than 20% cyclohexene could be achieved.

In comparison to organic additives, inorganic additives are deemed more effective for cyclohexene synthesis, such as the compounds Zn, Fe, Co, Ni, Cd, Ga, and In [10]. Up to now,  $\text{ZnSO}_4$  has been considered the most suitable choice [11], and it has been successfully industrialized by Asahi Kasei for the selective hydrogenation of benzene to cyclohexene using a Ru-based catalyst. Up to 80% selectivity and 32% yield toward cyclohexene production have been achieved [11,13]. In addition, a 53.8% cyclohexene yield was reported by Liu et al. over Ru-Ce/SBA-15 in a 0.42 mol/L aqueous solution of  $\text{ZnSO}_4$  [14]. However, it is still not clear what exact role  $\text{ZnSO}_4$  plays in improving the selectivity toward cyclohexene generation. For instance, Struijk et al. [10] claimed that the chemisorbed  $\text{ZnSO}_4$  could improve the hydrophilicity of the Ru surface, resulting in the Ru being covered by a stagnant water layer. This could prohibit the adsorption of  $\text{H}_2$  and cyclohexene, preventing the further hydrogenation of cyclohexene to cyclohexane. On the other hand, it was suggested by Yuan et al. [15] and Wang et al. [16] that  $\text{Zn}^{2+}$  from  $\text{ZnSO}_4$  was reduced into metallic Zn by the spillover H on the Ru surface. The adsorption of cyclohexene and its further hydrogenation could be retarded with the existence of metallic Zn [14–17].

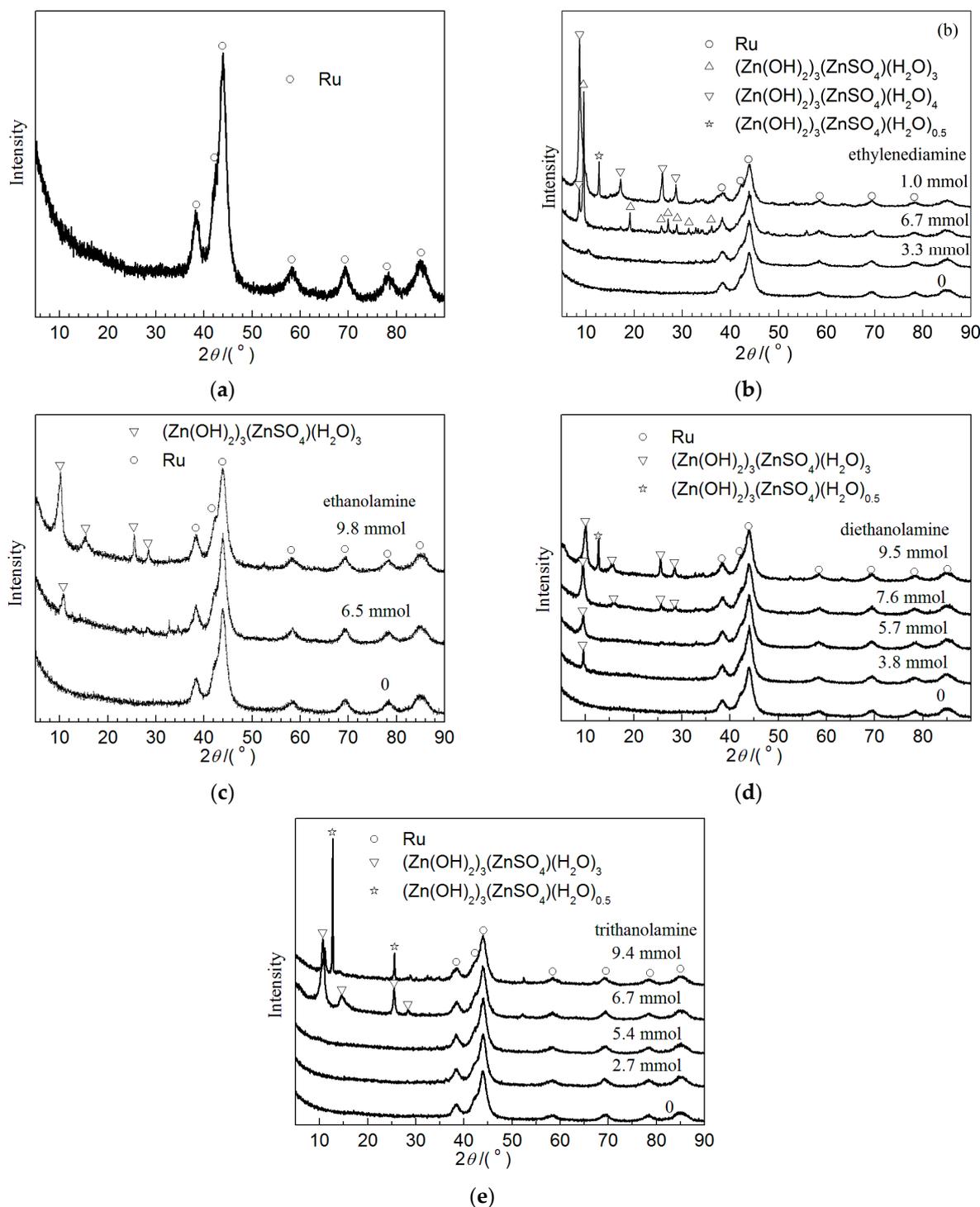
Additionally, amine is one of the most effective additives to improve the selectivity toward cyclohexene formation [18]. It was demonstrated by Fan et al. [19] that a 34.8% cyclohexene yield was obtained over Ru-Co-B/ $\gamma$ - $\text{Al}_2\text{O}_3$  with the addition of ethylenediamine in the presence of  $\text{ZnSO}_4$ , but no detailed mechanism was revealed about how the amines and  $\text{ZnSO}_4$  affect the catalytic selectivity toward cyclohexene formation over the Ru catalyst. Moreover, it was reported that the most active sites for cyclohexene generation were detected from Ru particles with a crystal size of 5 nm [20]. Therefore, a Ru catalyst with a crystal size of 5 nm was synthesized in this work. The effect of amines as additives was investigated on the selective hydrogenation of benzene toward cyclohexene generation in the presence of  $\text{ZnSO}_4$ . The fresh and used catalysts were thoroughly characterized via XRD, TEM, AES,  $\text{N}_2$ -sorption, FT-IR, and TPR—the mechanism for how amines and  $\text{ZnSO}_4$  influence catalytic activity and selectivity of the Ru catalyst is proposed. Furthermore, inert  $\text{ZrO}_2$  was introduced to the catalytic system to prevent the agglomeration of Ru particles, and the catalytic activity and stability of Ru were further evaluated as well.

## 2. Results and Discussion

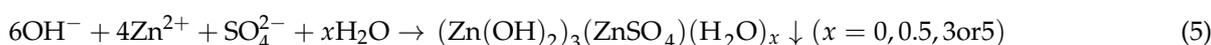
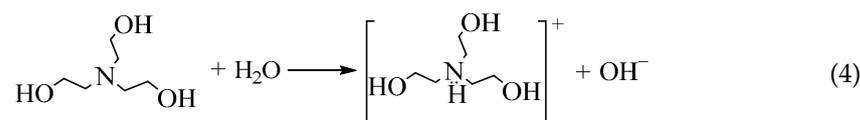
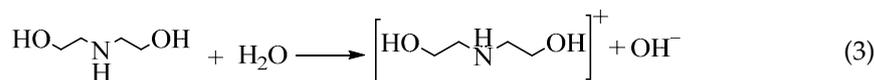
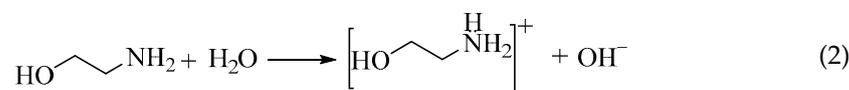
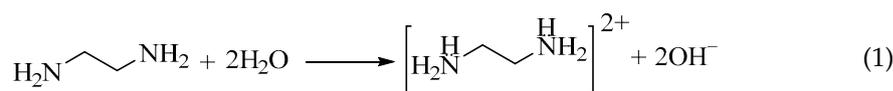
### 2.1. Catalyst Characterization

Figure 1 illustrates the XRD patterns of the Ru catalyst before and after the catalytic experiments with different amines applied as reaction additives. As can be observed in Figure 1a, only characteristic diffractions corresponding to metallic Ru of the hexagonal phase (JCPDS: 01-089-4903) are shown, demonstrating that Ru existed mainly in a metallic state during the hydrogenation reaction. On the other hand, when the applied ethane diamine was more than 6.7 mmol (Figure 1b), diffractions of  $(\text{Zn}(\text{OH})_2)_5(\text{ZnSO}_4)(\text{H}_2\text{O})_{0.5}$  (JCPDS: 00-044-0674),  $(\text{Zn}(\text{OH})_2)_5(\text{ZnSO}_4)(\text{H}_2\text{O})_3$  (JCPDS: 01-078-0247), and  $(\text{Zn}(\text{OH})_2)_5(\text{ZnSO}_4)(\text{H}_2\text{O})_4$  (JCPDS: 00-044-0673) were observed. Furthermore, when the added ethanol amine reached 6.5 mmol, reflection related to  $(\text{Zn}(\text{OH})_2)_5(\text{ZnSO}_4)(\text{H}_2\text{O})_3$  was detected (Figure 1c). Similarly, as shown in Figure 1d,e, with increasing amounts of added diethanolamine and triethanolamine, characteristic diffractions of  $(\text{Zn}(\text{OH})_2)_5(\text{ZnSO}_4)(\text{H}_2\text{O})_{0.5}$  and  $(\text{Zn}(\text{OH})_2)_5(\text{ZnSO}_4)(\text{H}_2\text{O})_3$  could be observed. It can be concluded that, despite the different types of added amines,  $(\text{Zn}(\text{OH})_2)_5(\text{ZnSO}_4)(\text{H}_2\text{O})_x$  ( $x = 0.5, 3, 4$ ) was formed during the reaction. This indicates that

the  $\text{OH}^-$  was generated via the basicity of the amines, which reacted with the  $\text{ZnSO}_4$  and  $\text{H}_2\text{O}$  to synthesize  $(\text{Zn}(\text{OH})_2)_5(\text{ZnSO}_4)(\text{H}_2\text{O})_x$  ( $x = 0.5, 3, 4$ ) based on the following equations. Hence, with the increasing amounts of applied amines, more  $(\text{Zn}(\text{OH})_2)_5(\text{ZnSO}_4)(\text{H}_2\text{O})_x$  ( $x = 0.5, 3, 4$ ) could be synthesized, leading to the enhanced intensity of the corresponding reflections of  $(\text{Zn}(\text{OH})_2)_5(\text{ZnSO}_4)(\text{H}_2\text{O})_x$  ( $x = 0.5, 3, 4$ ).



**Figure 1.** XRD patterns of Ru catalyst after the hydrogenation with amines as additives: (a) Fresh Ru catalysts, (b) ethylenediamine, (c) ethanolamine, (d) triethanolamine, and (e) diethanolamine.



In addition, the Ru crystallite size was obtained using a diffraction at  $44.0^\circ$ , which is shown in Table 1. As can be seen, the crystallite size of the fresh Ru catalyst was calculated to be 4.7 nm. After catalytic experiments with the addition of amines, the Ru crystallite size was still found to be around 4–5 nm, indicating that no obvious effect on the crystallite size of Ru was caused by the added amines.

**Table 1.** Elemental analysis and the crystallite size of Ru catalyst as well as the pH value of slurry before and after catalytic experiments when applying different amines as additives.

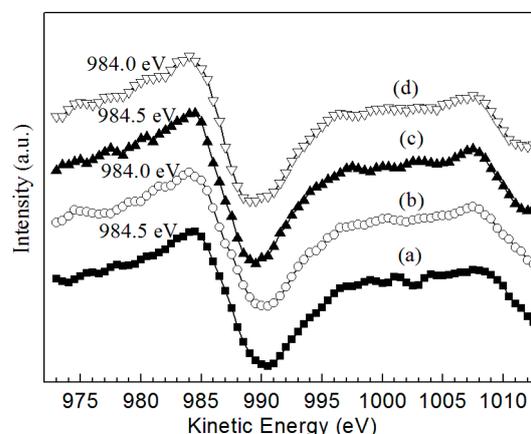
Amines	n(Zn)/n(Ru) (mol/mol)	n(S)/n(Ru) (mol/mol)	pH Value	Ru Crystallite Size (nm)
Ru catalyst	0	0		4.7
Blank <sup>a</sup>	0.0313	0.0026	5.53	4.5
3.3 mmol ethylenediamine <sup>a</sup>	0.2133	0.0159	6.03	4.3
6.7 mmol ethylenediamine <sup>a</sup>	0.5155	0.0593	6.04	4.3
1.0 mmol ethylenediamine <sup>a</sup>	0.8090	0.0877	6.28	5.0
6.5 mmol ethanolamine <sup>a</sup>	0.2535	0.0127	6.00	4.1
9.8 mmol ethanolamine <sup>a</sup>	0.3694	0.0403	6.20	4.9
3.8 mmol diethanolamine <sup>a</sup>	0.1597	0.0117	6.04	4.8
5.7 mmol diethanolamine <sup>a</sup>	0.2042	0.0184	6.02	4.8
7.6 mmol diethanolamine <sup>a</sup>	0.2695	0.0202	6.17	4.5
7.6 mmol diethanolamine <sup>b</sup>	0	0	10.57	4.6
9.5 mmol diethanolamine <sup>a</sup>	0.4150	0.0450	5.98	4.6
2.7 mmol triethanolamine <sup>a</sup>	0.1300	0.0061	6.25	4.5
5.4 mmol triethanolamine <sup>a</sup>	0.1337	0.0066	6.21	4.8
6.7 mmol triethanolamine <sup>a</sup>	0.2576	0.0181	6.16	4.7
9.4 mmol triethanolamine <sup>a</sup>	0.3488	0.0238	6.19	4.6

<sup>a</sup> Reaction conditions: 1.96 g catalyst, 280 mL of 0.6 mol/L  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  aqueous solution, 5 MPa  $\text{H}_2$ , and  $150^\circ\text{C}$ .

<sup>b</sup> In the absence of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ .

Figure 2 demonstrates the Auger electron kinetic energy of Zn LMM for the Ru catalyst after catalytic experiments with the addition of amines. In the presence of  $\text{ZnSO}_4$ , 984.5 eV, 984.0 eV, 984.5 eV, and 984.0 eV were observed for the Auger electron kinetic energy of Zn LMM of the Ru catalyst when applying ethylenediamine, ethanolamine, diethanolamine, and triethanolamine, respectively. This is consistent with that reported for  $\text{Zn}^{2+}$  of PtZn/C [21]. Moreover, as given in Table 1, the pH value of the slurry was around 6.0 with the presence of  $\text{ZnSO}_4$  after the catalytic experiments, suggesting that the slurry was acidic due to the hydrolysis of  $\text{ZnSO}_4$ . It is deemed that, under the reaction condition (i.e., 423 K), the slurry was more acidic, in which metallic Zn could hardly exist.

Therefore, it could be established that Zn on the Ru surface existed as  $\text{Zn}^{2+}$ , which is in agreement with the XRD results.

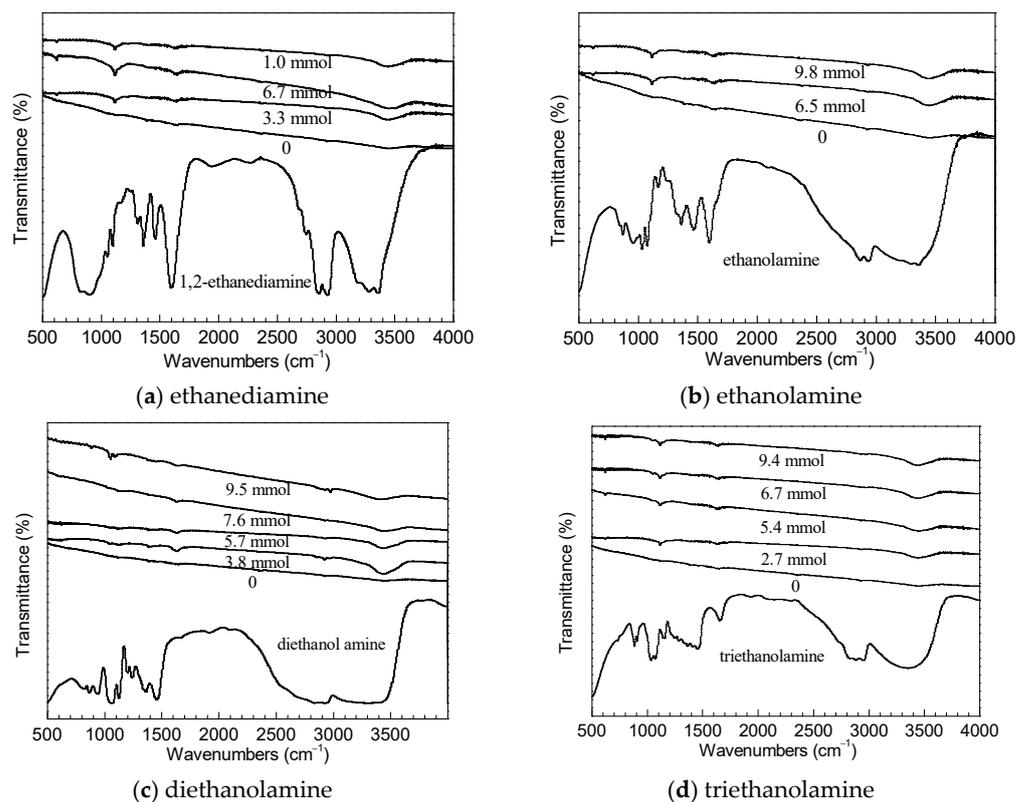


**Figure 2.** Auger electron kinetic energy of Zn LMM for Ru catalyst after catalytic experiments with the addition of amines in the presence of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ : (a) 6.7 mmol ethylenediamine, (b) 6.5 mmol ethanolamine, (c) 5.7 mmol diethanolamine, and (d) 6.7 mmol triethanolamine.

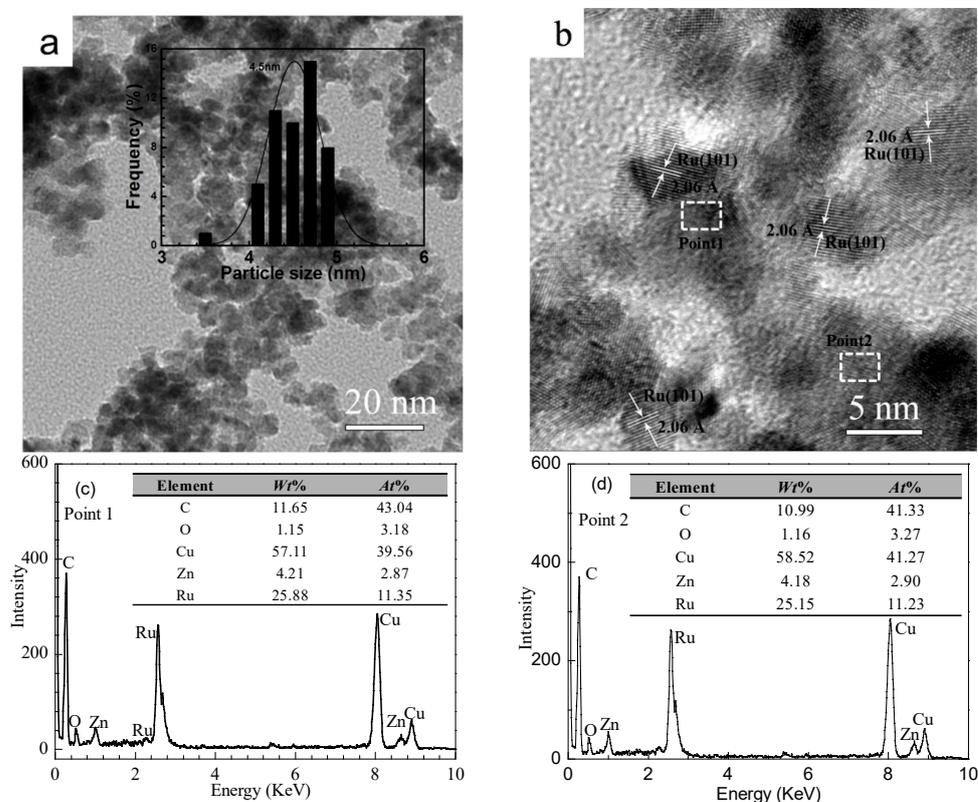
The elemental analyses of the Ru catalyst before and after the catalytic experiments are given in Table 1. As expected, neither Zn nor S was detected on the fresh Ru catalyst or spent Ru catalyst without the addition of  $\text{ZnSO}_4$ . On the other hand, when only  $\text{ZnSO}_4$  was added, the molar ratio of Zn/Ru and S/Ru over the spent catalyst was quite low, e.g., 0.0313 and 0.0026, respectively. This could be attributed to the fact that a small amount of basic zinc sulfate was generated from the hydrolysis of  $\text{ZnSO}_4$  [22]. Furthermore, when amines were also applied together with  $\text{ZnSO}_4$ , significant increases in the molar ratios of Zn/Ru and S/Ru were observed by enhancing the amount of added amine. This indicates that more  $(\text{Zn}(\text{OH})_2)_5(\text{ZnSO}_4)(\text{H}_2\text{O})_x$  ( $x = 0.5, 3, 4$ ) was adsorbed on the Ru surface. Moreover, as additives, 6.5 mmol ethanolamine, 5.7 mmol diethanolamine, and 6.7 mmol triethanolamine contained a comparable number of amino groups, and the amount of generated  $(\text{Zn}(\text{OH})_2)_5(\text{ZnSO}_4)(\text{H}_2\text{O})_x$  ( $x = 0.5, 3, 4$ ) was also comparable. Hence, the molar ratios of Zn/Ru and S/Ru were close as well. When 6.7 mmol ethanediamine was applied as the additive, the number of added amino groups was twice that provided by the other three kinds of amine. Thus, the amount of formed  $(\text{Zn}(\text{OH})_2)_5(\text{ZnSO}_4)(\text{H}_2\text{O})_x$  ( $x = 0.5, 3, 4$ ) was twice higher than that obtained for ethanolamine, diethanolamine, and triethanolamine. This is also in good agreement with the proposed equations.

Figure 3 shows the FT-IR spectra of the Ru catalyst after catalytic experiments with the addition of amines in the presence of  $\text{ZnSO}_4$ . As can be seen, with increasing the amount of applied amines, no typical functional group of the added amines was observed. This suggests that the added amines mainly existed as ammonium sulfate in the slurry, which could hardly be adsorbed on the Ru surface. A similar observation was also reported by Struijk et al. [8] that organic additives could not be adsorbed on the Ru surface.

Figure 4a illustrates the TEM images and particle size distribution of the spent Ru catalyst after catalytic experiments with the addition of 7.6 mmol diethanolamine in the presence of  $\text{ZnSO}_4$ . It can be observed that Ru particles were in a circular or elliptical shape. The particle size of the sample was around 4.5 nm, which is in agreement with that calculated from the XRD result. In addition, as shown in Figure 4b, the lattice fringe of Ru was very clear, and the average inter-planar spacing was 0.20 nm. This is attributed to the hexagonal phase of metallic Ru (101) [3,23]. Furthermore, Figure 4c and d show the EDS spectra of the two selected points in Figure 4b, respectively. It can be seen that the content of Zn and Ru in both points was extremely comparable, implying that the formed  $(\text{Zn}(\text{OH})_2)_5(\text{ZnSO}_4)(\text{H}_2\text{O})_x$  ( $x = 0.5, 3, 4$ ) was uniformly dispersed on the Ru surface.



**Figure 3.** FT-IR spectra of Ru catalyst after catalytic experiments with the addition of amines in the presence of  $\text{ZnSO}_4$ . (a) ethylenediamine; (b) ethanolamine; (c) diethanolamine; (d) triethanolamine.



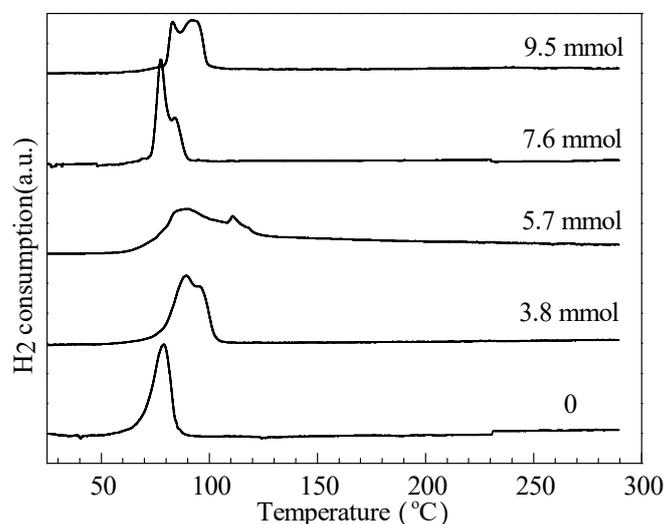
**Figure 4.** TEM image and particle size distribution (a), HTEM image (b), and EDS spectra (c,d) of the spent Ru catalyst after catalytic experiments with the addition of 7.6 mmol diethanolamine in the presence of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ .

Table 2 provides the textural properties of the Ru catalyst after the catalytic experiments involving the application of different amounts of diethanolamine as an additive in the presence of  $\text{ZnSO}_4$ . A clear tendency of decline was observed for the specific surface area, average pore size, and pore volume. This was mainly rationalized in terms that the synthesized  $(\text{Zn}(\text{OH})_2)_5(\text{ZnSO}_4)(\text{H}_2\text{O})_x$  ( $x = 0.5, 3, 4$ ) was transferred and blocked some of the pores of the Ru catalyst.

**Table 2.** Texture properties of Ru catalysts with applying different amounts of diethanolamine as an additive in the presence of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ , including specific surface area ( $A$ ), average pore size ( $d$ ), and pore volume ( $V$ ).

Additive	$A/(\text{m}^2/\text{g})$	$d/\text{nm}$	$V/(\text{cm}^3/\text{g})$
Blank	70	10.44	0.191
0.4 g diethanol amine	60	8.94	0.134
0.6 g diethanol amine	59	10.21	0.152
0.8 g diethanol amine	50	10.41	0.130
1.0 g diethanol amine	49	8.11	0.099

Figure 5 demonstrates the TPR profiles of the Ru catalyst after catalytic experiments involving the application of different amounts of diethanolamine as an additive in the presence of  $\text{ZnSO}_4$ . A reduction peak with the shoulder peak can be observed at the range between 323–373 K, which corresponds to the reduction of  $\text{Ru}^{4+} \rightarrow \text{Ru}^{3+} \rightarrow \text{Ru}^{2+} \rightarrow \text{Ru}^0$  [24]. Hence, there could be two or three shoulder peaks for each sample. Noteworthy, the reduction temperature of Ru over all tested samples was below 423 K, indicating that the Ru existed in a metallic state under the reaction conditions (i.e., 423 K, 5 MPa  $\text{H}_2$ ). More importantly, no reduction peak of  $\text{Zn}^{2+}$  was observed until 573 K, suggesting that Zn could not be reduced during the catalytic experiments.



**Figure 5.** TPR profiles of Ru catalyst after catalytic experiments involving the application of different amounts of diethanolamine as an additive in the presence of  $\text{ZnSO}_4$ .

## 2.2. Catalytic Performance

Catalytic activity towards benzene conversion and cyclohexene formation over the Ru catalyst when applying different amines are illustrated in Table 3. In the presence of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ , an obvious decrease in catalytic activity towards benzene conversion was noticed with raising the amount of added amines. Meanwhile, an enhancement of the selectivity to cyclohexene synthesis was observed. The highest cyclohexene yield of 44.5%, 56.9%, 56.7%, and 52.4% were obtained by applying 3.3 mmol ethanediamine, 6.5 mmol ethanolamine, 5.7 mmol diethanolamine, and 6.7 mmol triethanolamine, respectively. In

comparison to that achieved by adding  $\text{ZnSO}_4$  only (e.g., 33% yield of cyclohexene), the catalytic activity towards cyclohexene formation is significantly improved by using amines as additives in the presence of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ . On the other hand, in the absence of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ , a complete conversion of benzene and no cyclohexene was obtained with the addition of 7.6 mmol diethanolamine. This suggests that selectivity towards cyclohexene formation could not be improved by the amines as the additive only. In addition, it is important to address that, considering the difficulty of the further separation of cyclohexene from the slurry in industrial applications, catalytic selectivity and activity towards cyclohexene formation demanded to be no less than 80% and 40%, respectively [13]. With respect to this demand, 7.6 mmol diethanolamine was selected for further investigation.

**Table 3.** Effect of amines as additives on the selective hydrogenation of benzene towards cyclohexene formation over Ru catalyst.

Amines	Conversion (%) <sup>2</sup>	Selectivity (%) <sup>2</sup>	Yield (%) <sup>2</sup>	Time (min) <sup>2</sup>
Blank test <sup>1</sup>	70.7	46.7	33.0	5
3.3 mmol ethanediamine <sup>1</sup>	92.7	48.0	44.5	15
6.7 mmol ethanediamine <sup>1</sup>	35.5	86.4	30.7	25
10.0 mmol ethanediamine <sup>1</sup>	28.7	86.9	24.9	25
6.5 mmol ethanolamine <sup>1</sup>	85.0	66.9	56.9	25
9.8 mmol ethanolamine <sup>1</sup>	31.1	86.0	26.8	25
3.8 mmol diethanolamine <sup>1</sup>	90.2	54.2	48.8	15
5.7 mmol diethanolamine <sup>1</sup>	84.6	67.1	56.7	20
7.6 mmol diethanolamine <sup>1</sup>	57.0	84.5	48.6	25
7.6 mmol diethanolamine <sup>3</sup>	100	0	0	5
9.5 mmol diethanolamine <sup>1</sup>	29.1	88.5	25.8	25
2.7 mmol triethanolamine <sup>1</sup>	94.3	44.0	41.5	10
5.4 mmol triethanolamine <sup>1</sup>	90.6	53.9	48.9	15
6.7 mmol triethanolamine <sup>1</sup>	69.9	75.1	52.4	25
9.4 mmol triethanolamine <sup>1</sup>	40.2	84.5	34.0	25

<sup>1</sup> Blank test: 1.96 g catalyst, 280 mL of 0.6 mol/L  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  aqueous solution, 5 MPa  $\text{H}_2$ , and 150 °C. <sup>2</sup> Values recorded at the maximum yield of cyclohexene. <sup>3</sup> In the absence of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ .

In order to further investigate what roles the amine and  $\text{ZnSO}_4$  play during the reaction, three experiments (test 2, test 3, and test 4) were intentionally designed and conducted (Table 4). After the catalytic experiment with the presence of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  and 7.6 mmol diethanolamine (test 1), the aqueous phase, the organic phase, and the used Ru catalyst were separated, and the used Ru catalyst was washed until no  $\text{Zn}^{2+}$  could be detected. Then, the aqueous phase (including amine salt) and the used Ru catalyst were applied for the following three tests: test 2, catalytic experiment with a fresh Ru catalyst and the aqueous phase (including amine salt); test 3, catalytic experiment with the used Ru catalyst and another 280 mL of fresh water in the absence of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ; test 4, catalytic experiment with the used Ru catalyst and another 280 mL of fresh water in the presence of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ . The experimental results are shown in Figure 6. As can be seen, the catalytic activity towards benzene conversion and selectivity towards cyclohexene generation of test 2 is the same as that achieved for the blank test. This suggests that the amine salts in the aqueous phase play no role in improving the cyclohexene selectivity. On the other hand, 93.1% of cyclohexene selectivity and 2.4% of benzene conversion were obtained for test 3 after 25 min of reaction time, indicating that the chemisorbed  $(\text{Zn}(\text{OH})_2)_5(\text{ZnSO}_4)(\text{H}_2\text{O})_x$  ( $x = 0.5, 3, 4$ ) was the key to the enhancement of cyclohexene selectivity. Moreover, for test 4, 84.7% of cyclohexene selectivity and 55.0% benzene conversion were achieved after 25 min of reaction time, which is comparable to that achieved with 7.6 mmol of diethanolamine in the presence of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ . This demonstrates that benzene could be activated by the  $\text{Zn}^{2+}$  in the slurry, increasing the catalytic activity towards benzene conversion over the Ru catalyst.

**Table 4.** Reaction substrate of each designed experiment.

Experiment <sup>a</sup>	Reaction Substrate
Blank	1.96 g catalyst, 280 mL of 0.6 mol/L ZnSO <sub>4</sub> ·7H <sub>2</sub> O aqueous solution
Test1	1.96 g catalyst, 280 mL of 0.6 mol/L ZnSO <sub>4</sub> ·7H <sub>2</sub> O aqueous solution, 7.6 mmol diethanolamine
Test2	Slurry in Test 1 (including amine and 280 mL of 0.6 mol/L ZnSO <sub>4</sub> ·7H <sub>2</sub> O aqueous solution), 1.96 g catalyst
Test3	Spent catalyst in Test 1 (covered with chemisorbed Zn salts), 280 mL H <sub>2</sub> O
Test4	Spent catalyst in Test 1 (covered with chemisorbed Zn salts), 280 mL of 0.6 mol/L ZnSO <sub>4</sub> ·7H <sub>2</sub> O aqueous solution

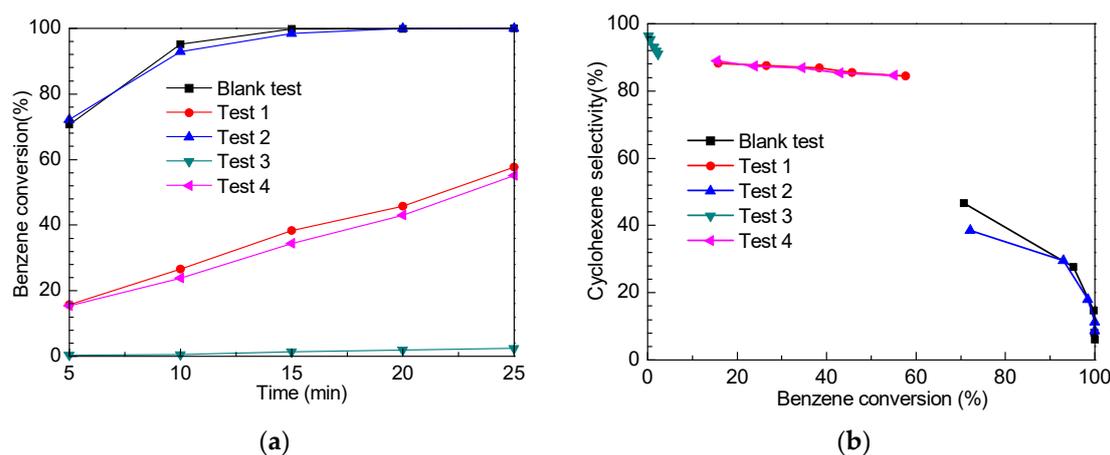
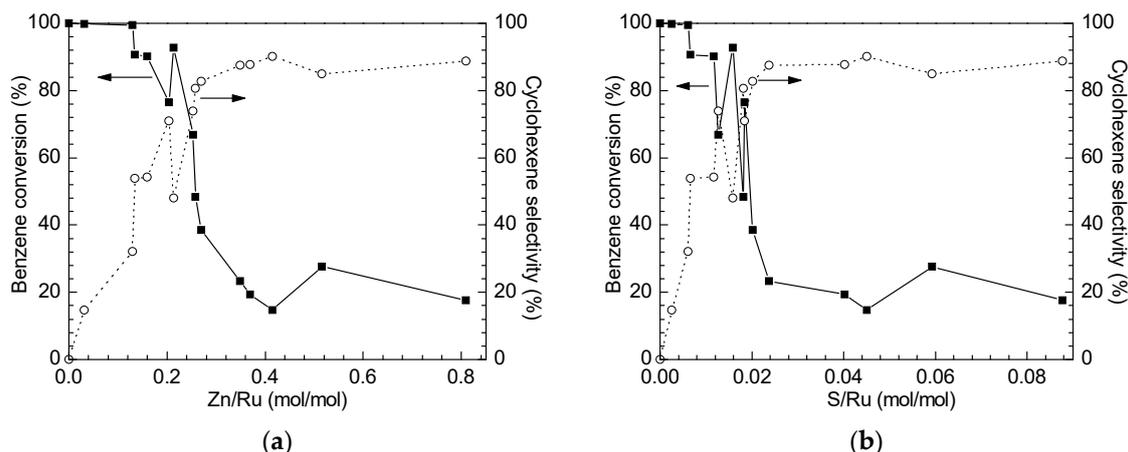
<sup>a</sup> 5 MPa H<sub>2</sub>, 150 °C.**Figure 6.** Benzene conversion (a) and cyclohexene selectivity (b) over Ru catalyst after 25 min of reaction time under different conditions.

Figure 7 shows the benzene conversion and cyclohexene selectivity as a function of the molar ratio of Zn/Ru (a) as well as S/Ru (b) after 15 min of reaction time. The higher molar ratios of Zn/Ru and S/Ru suggest that more  $(\text{Zn}(\text{OH})_2)_5(\text{ZnSO}_4)(\text{H}_2\text{O})_x$  ( $x = 0.5, 3, 4$ ) was chemisorbed on the Ru surface. As can be seen, with increasing the molar ratios of Zn/Ru and S/Ru, a lower benzene conversion and higher selectivity to cyclohexene were observed. When the molar ratios of Zn/Ru and S/Ru reached 0.42 and 0.045, respectively, the lowest benzene conversion and the highest cyclohexene selectivity were obtained. This indicates that the highest amount of  $(\text{Zn}(\text{OH})_2)_5(\text{ZnSO}_4)(\text{H}_2\text{O})_x$  ( $x = 0.5, 3, 4$ ) was chemisorbed on the Ru surface. Interestingly, with increasing the molar ratios of Zn/Ru and S/Ru, a slight decline in benzene conversion and enhancement of selectivity to cyclohexene was observed. This might be due to the fact that the excessively generated  $(\text{Zn}(\text{OH})_2)_5(\text{ZnSO}_4)(\text{H}_2\text{O})_x$  ( $x = 0.5, 3, 4$ ) could no longer be chemisorbed on the Ru surface, which further acts as an inert support. These results suggest that the catalytic activity towards cyclohexene synthesis is controlled by both the Ru catalyst as well as the chemisorbed  $(\text{Zn}(\text{OH})_2)_5(\text{ZnSO}_4)(\text{H}_2\text{O})_x$  ( $x = 0.5, 3, 4$ ).

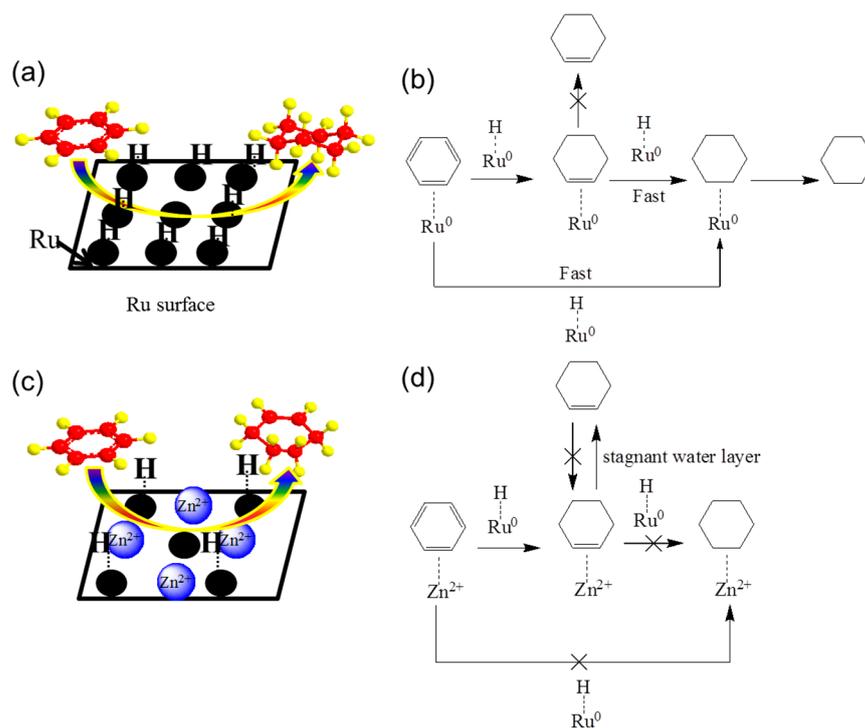
For further clarification,  $Ca$  and  $\eta\phi^2$  were calculated to prove the absence of diffusion limitations. It was found that  $Ca$  and  $\eta\phi^2$  were far less than 0.05 and 0.1, respectively. This indicates that the reaction is taking place under the kinetic control [25,26]. Furthermore, in our previous study [27], the pure Ru catalysts with different particle sizes and amounts were investigated for benzene hydrogenation. Only cyclohexane was generated over the pure Ru catalysts. These observations further prove that the improvement in cyclohexene yield cannot be attributed to the diffusion limitation but mainly due to the chemisorbed  $(\text{Zn}(\text{OH})_2)_5(\text{ZnSO}_4)(\text{H}_2\text{O})_x$  ( $x = 0.5, 3, 4$ ).



**Figure 7.** Benzene conversion (black square) and cyclohexene selectivity (white square) as a function of molar ratio of Zn/Ru (a) as well as S/Ru (b) after 15 min of reaction time.

Based on the aforementioned characterization and experimental results, the effect of the chemisorbed  $(\text{Zn}(\text{OH})_2)_5(\text{ZnSO}_4)(\text{H}_2\text{O})_x$  ( $x = 0.5, 3, 4$ ) on improving the cyclohexene formation was proposed. It has been established that the hydrogenation of benzene includes two parallel reactions [28,29]. One is step-by-step, going through cyclohexadiene (which is extremely unstable and hard to detect) and hydrogenating cyclohexene to cyclohexane. The other is the direct hydrogenation of benzene to cyclohexane. Either way, both  $\text{H}_2$  and benzene were activated on the active sites of Ru. In addition, it was reported that  $\text{H}_2$  could easily be dissociated and adsorbed on the Ru surface [30,31], leading to that the activated benzene on Ru was surrounded by H atoms. Therefore, as shown in Figure 8a,b, without the chemisorbed  $(\text{Zn}(\text{OH})_2)_5(\text{ZnSO}_4)(\text{H}_2\text{O})_x$  ( $x = 0.5, 3, 4$ ), most of the benzene was directly hydrogenated to cyclohexane, and the formed cyclohexene was also further hydrogenated to cyclohexane. On the other hand, when  $(\text{Zn}(\text{OH})_2)_5(\text{ZnSO}_4)(\text{H}_2\text{O})_x$  ( $x = 0.5, 3, 4$ ) was chemisorbed on the Ru surface (Figure 8c), parts of the Ru-active sites were covered by  $\text{Zn}^{2+}$ . In such a case, it was not only lessened by the Ru-active sites for dissociation of  $\text{H}_2$  but also weakened the ability for dissociation of  $\text{H}_2$  by the contiguous Ru atoms [30,32]. This could significantly retard the complete hydrogenation of benzene to cyclohexane. In addition, although the chemisorbed  $(\text{Zn}(\text{OH})_2)_5(\text{ZnSO}_4)(\text{H}_2\text{O})_x$  ( $x = 0.5, 3, 4$ ) could hinder the activation of benzene by Ru, the benzene was able to be activated by the  $\text{Zn}^{2+}$  as well [33]. More importantly, a complex could be formed between cyclohexene and  $\text{Zn}^{2+}$  [3,11,12,14], stabilizing the generated cyclohexene and retarding its further hydrogenation to cyclohexane. Hence, the  $\text{Zn}^{2+}$ -activated benzene was mainly hydrogenated to cyclohexene. Furthermore, there is plenty of crystallized water in the chemisorbed  $(\text{Zn}(\text{OH})_2)_5(\text{ZnSO}_4)(\text{H}_2\text{O})_x$  ( $x = 0.5, 3, 4$ ), resulting in the formation of a stagnant water layer on the Ru surface. Since the solubility of cyclohexene in water is lower than benzene, the stagnant water layer is beneficial for the desorption of cyclohexene from the Ru surface and hinders its re-adsorption and further hydrogenation to cyclohexane [34]. As demonstrated in Figure 8d, the decline in catalytic activity towards benzene conversion and the increase in cyclohexene selectivity was mainly due to the chemisorbed  $(\text{Zn}(\text{OH})_2)_5(\text{ZnSO}_4)(\text{H}_2\text{O})_x$  ( $x = 0.5, 3, 4$ ) on the Ru surface.

Regarding the reusability of the Ru catalyst, the agglomeration of nano-Ru particles is deemed to be quite normal, resulting in a decrease in catalytic activity. It was reported that the agglomeration of nano-Ru particles could be hindered by the addition of metal oxides [11]. Plenty of metal oxides were tested as a support or dispersant for the partial hydrogenation of benzene over the Ru catalysts in our group. The highest yield of cyclohexene was achieved by applying  $\text{ZrO}_2$ . Hence, in the presence of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ , the effect of  $\text{ZrO}_2$  was investigated with 7.6 mmol diethanolamine. The catalytic activity towards benzene conversion and selectivity to cyclohexene is given in Table 5.



**Figure 8.** Effect of chemisorbed Zn<sup>2+</sup> on improving the cyclohexene formation. (a,b): hydrogenation of benzene on the pure Ru surface; (c,d): hydrogenation of benzene on the Ru surface chemisorbed with Zn<sup>2+</sup>.

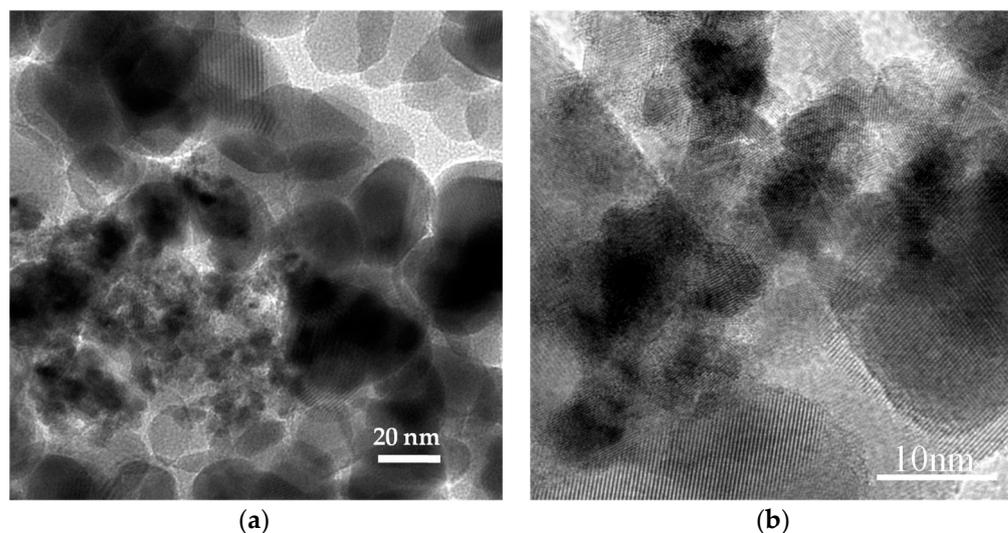
**Table 5.** Benzene conversion, cyclohexene selectivity, and yield over Ru catalysts with different amounts of ZrO<sub>2</sub> in the presence of ZnSO<sub>4</sub>·7H<sub>2</sub>O and dietholamine <sup>a</sup>.

ZrO <sub>2</sub> Dosage (g)	Benzene Conversion <sup>b</sup> (%)	Cyclohexenes Electivity <sup>b</sup> (%)	Cyclohexene Yield <sup>b</sup> (%)	Time <sup>b</sup> (min)
0	57.7	84.5	48.6	25
5	77.5	74.6	57.7	25
10	80.1	77.0	61.6	25
15	87.9	64.5	56.7	25
20	94.8	54.0	56.2	15

<sup>a</sup> Reaction conditions: 1.96 g catalyst, 280 mL of 0.6 mol/L ZnSO<sub>4</sub>·7H<sub>2</sub>O aqueous solution, 5 MPa H<sub>2</sub>, 423 K, and 7.6 mmol dietholamine. <sup>b</sup> Values recorded at the maximum yield of cyclohexene.

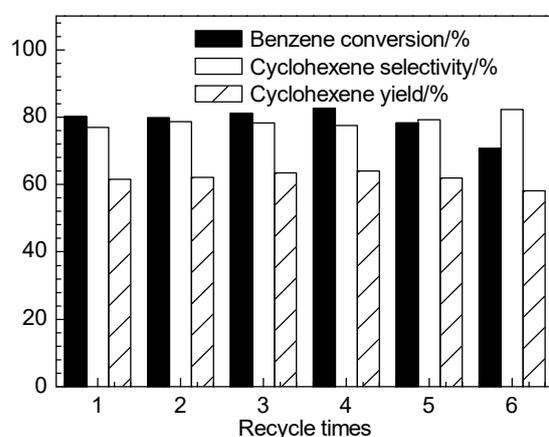
It is obvious that with increasing the dosage of ZrO<sub>2</sub>, an enhancement of benzene conversion and a decline in cyclohexene selectivity were observed. This can be attributed in terms of two reasons: (1) part of the generated (Zn(OH)<sub>2</sub>)<sub>5</sub>(ZnSO<sub>4</sub>)(H<sub>2</sub>O)<sub>x</sub> was chemisorbed on the ZrO<sub>2</sub>, decreasing the amount of chemisorbed (Zn(OH)<sub>2</sub>)<sub>5</sub>(ZnSO<sub>4</sub>)(H<sub>2</sub>O)<sub>x</sub> on the Ru surface. (2) The dispersion of Ru could be improved by the added ZrO<sub>2</sub>; hence, the coverage of (Zn(OH)<sub>2</sub>)<sub>5</sub>(ZnSO<sub>4</sub>)(H<sub>2</sub>O)<sub>x</sub> on the Ru surface was declined accordingly. When 10 g of ZrO<sub>2</sub> was applied, 80.1% of benzene conversion and 77.0% of cyclohexene selectivity were obtained after 25 min of reaction time. A total of 61.6% of cyclohexene yield is one of the highest levels ever reported [11,12]. More importantly, the selectivity of 77.0% is quite promising, which does not increase the cost for further separation of cyclohexene.

Figure 9 illustrates the TEM and HTEM images of the Ru catalyst after the catalytic experiment with the presence of ZrO<sub>2</sub>. It can be clearly observed that Ru crystallite was uniformly distributed on the ZrO<sub>2</sub>. This could not only improve the activity of Ru but also prevent the agglomeration of nano-Ru particles. On the other hand, as shown in Figure 4b, a non-uniform distribution of Ru was observed without applying ZrO<sub>2</sub>.



**Figure 9.** TEM (a) and HTEM (b) images of Ru catalyst after the catalytic experiment with the presence of  $ZrO_2$ .

Figure 10 shows the reusability of the Ru catalyst with the addition of 7.5 mmol diethanolamine and 10 g of  $ZrO_2$  in the presence of  $ZnSO_4$ . A slight decrease in the catalytic towards benzene conversion and cyclohexene yield can be observed. This might be due to the loss of catalyst during each run. However, 82.3% of selectivity and 58.1% of yield toward cyclohexene formation could be achieved after six recycle times, indicating the promising stability of this catalytic system. By applying the continuous regeneration process, the high activity and selectivity towards cyclohexene production could be sustained for industrial application [13].



**Figure 10.** Benzene conversion, cyclohexene selectivity, and yield over the Ru catalyst in the six recycle times. Reaction conditions: 1.96 g catalyst, 10 g  $ZrO_2$ , 280 mL of 0.6 mol/L  $ZnSO_4 \cdot 7H_2O$  aqueous solution, 5 MPa  $H_2$ , 150 °C, and 7.6 mmol diethanolamine.

### 3. Materials and Methods

#### 3.1. Preparation of Catalysts

The Ru catalyst was prepared as follows: 30.0 g of  $RuCl_3 \cdot 3H_2O$  was dissolved in distilled water. Then, a certain amount of NaOH solution was added with continuous stirring. After an adequate reaction between  $RuCl_3 \cdot 3H_2O$  and NaOH, the solid was filtered and washed three times using distilled water. Subsequently, the solid was dispersed in 600 mL of deionized water, followed by a reduction procedure in a 1000 mL Hastelloy autoclave (GS-1 from Weihai Chemical Machinery Co., Ltd., Dalian, China) under 5.0 MPa of hydrogen and a stirring

speed of 800 rpm at 423 K. After 3 h of reduction and cooling to room temperature, the fresh catalysts were obtained by washing to neutral and vacuum-dried.

### 3.2. Catalytic Experimental Procedure

All catalytic experiments were carried out in a 1000 mL GS-1 type Hastelloy autoclave (GS-1 from Weihai Chemical Machinery Co., Ltd., Dalian, China). Prior to the reaction, 1.9 g of Ru catalyst, a certain amount of amines, 49.2 g  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ , and 280 mL of  $\text{H}_2\text{O}$  were added into the autoclave. Then, the reactor was heated to 423 K under 5.0 MPa of  $\text{H}_2$  with a stirring speed of 800 rpm, followed by adding 140 mL of benzene and adjusting the stirring speed to 1400 rpm to eliminate the mass transfer limitation. Subsequently, the liquid samples were taken periodically every 5 min. All withdrawn samples were analyzed by GC-FID (GC-1690 from Hangzhou Kexiao Chemical Equipment Co., Ltd., Hangzhou, China). The benzene conversion and selectivity towards cyclohexene were calculated with the calibration area normalization method. After each reaction, the catalyst sample was separated from the organic phase, then filtered and washed until no  $\text{Zn}^{2+}$  could be detected in the filtrate. Then, the catalyst was vacuum-dried at 333 K for further characterization. It was denoted as a "Blank test" without the addition of any amines or  $\text{ZrO}_2$ .

### 3.3. Catalyst Characterization Methods

X-ray diffraction (XRD) patterns were recorded using a diffracted intensity of  $\text{Cu-K}\alpha$  radiation ( $\lambda = 0.15418$  nm) via an X'Pert Pro instrument (PAN Nallytical, Almelo, The Netherlands). The scanned range of  $2\theta$  was set from  $5^\circ$  to  $90^\circ$  with a step size of  $0.03^\circ$ . The crystallite size of the samples was calculated via Scherrer's equation. Moreover, the kinetic energy of Zn LMM electrons was analyzed with a ULVAC PHI-700 system (ULVAC-PHI, Inc., Chigasaki, Japan) under  $5.2 \times 10^{-7}$  Pa using the thermos-oxidative  $\text{SiO}_2/\text{Si}$  as the standard sample. The incident angle of the electron gun was  $30^\circ$ , with a high voltage of 10 kV as well as an energy resolution of 0.1%. The spectra were recorded after  $\text{Ar}^+$  pretreatment of sputtering for 2 min. In addition, elemental analysis was conducted via X-ray fluorescence (XRF) using a S4 Pioneer instrument from Bruker AXS, Karlsruhe, Germany. The molar ratio was calculated based on the element content detected. Furthermore, the morphology of the catalyst surface was observed by a JEOL JEM 2100 transmission electron microscope (TEM, Akishima, Japan). FT-IR (Nicolet IR 200 from Thermo Fisher Scientific, Waltham, MA, USA). Spectra were recorded from a wavenumber of  $4000\sim 500$   $\text{cm}^{-1}$  using a KBr disk (Sinopharm Chemical ReagentCo., Ltd., Shanghai, China) as a carrier. Textural properties were analyzed via  $\text{N}_2$ -sorption using a Nova 1000e-Physisorption Analyzer from Quanta Chrome Company (Boynton Beach, FL, USA). Moreover, temperature programmed reduction (TPR) was conducted by a self-constructed device. The sample was firstly oxidized by the air/ $\text{N}_2$  mixed gas for 2 h at 353 K, followed by purification with Ar for 3 h. Then, 5%  $\text{H}_2/\text{N}_2$  (30 mL/min) and 10 K/min of the temperature rising rate were applied during analysis.

## 4. Conclusions

Amines as additives could significantly improve the catalytic selectivity towards cyclohexene formation in the presence of  $\text{ZnSO}_4$ . This was attributed to the formation of  $(\text{Zn}(\text{OH})_2)_5(\text{ZnSO}_4)(\text{H}_2\text{O})_x$  ( $x = 0.5, 3$  or  $4$ ) through the reaction between  $\text{ZnSO}_4$  and amines, which could be chemisorbed on the Ru surface. The chemisorbed  $(\text{Zn}(\text{OH})_2)_5(\text{ZnSO}_4)(\text{H}_2\text{O})_x$  ( $x = 0.5, 3, 4$ ) not only hinders the activation of benzene on Ru by occupying parts of active sites but also stabilizes the generated cyclohexene by forming a complex. This leads to retarding the formation of cyclohexane from the complete hydrogenation of benzene, as well as preventing the further hydrogenation of cyclohexene to cyclohexane. Moreover, the chemisorbed  $(\text{Zn}(\text{OH})_2)_5(\text{ZnSO}_4)(\text{H}_2\text{O})_x$  contained plenty of crystal water, for which a stagnant water layer could be formed on the Ru surface. This accelerates the desorption of cyclohexene from the Ru surface and hinders the further hydrogenation of cyclohexene to cyclohexane. Therefore, with the presence of  $\text{ZnSO}_4$ , the amount of chemisorbed

$(\text{Zn}(\text{OH})_2)_5(\text{ZnSO}_4)(\text{H}_2\text{O})_x$  would increase with enhancing the amount of added amines, leading to a decline in catalytic activity towards benzene conversion and improving the selectivity towards cyclohexene generation. When 0.8 g of diethanolamine and 10 g of  $\text{ZrO}_2$  were applied, the highest cyclohexene yield of 61.6% and 77.0% of benzene conversion was achieved over the Ru catalyst. Promising stability was demonstrated after six runs of catalytic experiments without regeneration. These results demonstrate that the chemisorbed salts could alter the reaction mechanism of a metal catalyst, improving the relative selectivity. Future investigations should focus on how the chemisorbed salts alter the reaction mechanism.

**Author Contributions:** H.S. and Z.C. were responsible for designing the experiments and manuscript preparation. W.Z. and X.W. were responsible for conducting the experiments and data analysis. Z.P. was responsible for making the figures. All authors have read and agreed to the published version of the manuscript.

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**Data Availability Statement:** Data are contained within the article.

**Conflicts of Interest:** The authors declare no conflicts of interest.

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