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Article

Ru-Zn catalysts for selective hydrogenation of benzene using coprecipitation in low alkalinity

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ABSTRACT

Several unsupported Ru-Zn catalysts were successfully prepared using the coprecipitation method under low alkaline conditions, and their catalytic performance was evaluated for the selective liquid-phase hydrogenation of benzene. The effect of the amount of $ZnCl_2$ added to the coprecipitation solution on the physical and catalytic properties of the Ru-Zn catalysts was studied whilst keeping the amount of the NaOH precipitant constant. The properties of the resulting catalysts were characterized by N_2 adsorption, X-ray diffraction, and temperature-programmed reduction. The effects of the stirring rate and the amount of $ZnSO_4$ additive on the catalytic properties of the Ru-Zn catalysts were investigated using the optimal Zn content. The recyclability of the optimal Ru-Zn catalyst was also explored. The results revealed that the optimal Zn content for the Ru-Zn catalysts was 16.7 wt%, and the selectivity for cyclohexene could reach up to 80% (yield > 45%) when the benzene conversion was 57% in an aqueous solution of $ZnSO_4$ (0.45 mol/L) under the optimal reaction conditions (i.e., hastelloy reactor, 1200 r/min, 150 °C and 5 MPa of H_2 pressure). The presence of ZnO crystals in the Ru catalysts was found to be critical to obtaining high selectivity for cyclohexene (>80%). The Ru-Zn catalysts prepared under the low alkaline conditions also showed good stability, which indicates that they could potentially be used for industrial application.

1. Introduction

Cyclohexene is an important intermediate in the fine chemicals industry, where it is used for the construction of many organic chemicals, and this compound is therefore considered to be of significant commercial importance. The production of cyclohexanol from benzene via cyclohexene is a green process, but the commercialization of this process is considered by many scientists in the fine chemicals industry to be difficult because the partial hydrogenation of benzene is thermodynamically unfavorable. Several innovative techniques, however, have been developed to allow for the efficient partial hydrogenation of benzene. Numerous studies have been conducted towards the development of new methods for the selective hydrogenation of benzene to cyclohexene, and Ru-based catalysts have been being used in the majority of these cases because they give the best yield of cyclohexene. The first reported example of the Ru-based catalyst for the hydrogenation of benzene was provided by Hartog et al. [1] in 1963. In this particular case, benzene was hydrogenated over a Ru-black catalyst in the presence of an aliphatic alcohol, but the yield of cyclohexene was reported to be as low as 2.2%. The first encouraging result for this reaction was obtained by Drinkard et al. [2], who reported that a much higher yield (30%) of cyclohexene could be achieved when benzene was hydrogenated over a Ru-based catalyst in the presence of water, and this basic idea

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was subsequently developed further by several other researchers [3–30]. The effects of numerous promoters and co-catalysts on this reaction have also been studied in detail [5–8].

In 1988, Nagahara et al. [8] of Asahi-Kasei Chemical Co., Ltd reported the synthesis of an efficient catalyst composed of a Ru-black promoted with ZnO that provided a high yield of cyclohexene (48%) from benzene with a selectivity of 80%. This particular process was carried out in a mechanically agitated tetraphase reactor (i.e., oil phase: benzene; aqueous phase: $ZnSO_4$ aqueous solution; gas phase: H_2; and solid phase: Ru-based catalyst) at 150 °C under 5 MPa of H_2 pressure in the presence of suspended ZrO_2, which was added to avoid the agglomeration of the catalyst. Based on this process, Asahi-Kasei developed the first commercial plant for the product of cyclohexene in 1990 that produced 60 000 t of this material per year via the selective hydrogenation of benzene.

Supported [1–24] and unsupported [25–33] Ru-based catalysts have been investigated extensively. Although numerous reports have been published in the literature pertaining to the development and application of supported Ru-based catalysts, there have been no reports, to the best of our knowledge, concerning the commercial application of these catalysts for the selective hydrogenation of benzene. Considerable research efforts have been devoted to the development of unsupported Ru-based catalysts by Liu and his team in China [16–24]. To date, Ru-black promoted with ZnO (designated as Ru-Zn) has been widely used by numerous researchers for the selective hydrogenation of benzene, where it has been reported to exhibit a high level of reactivity [6–11,20,22]. Ru-Zn catalysts have been prepared by a variety of different methods, including coprecipitation [6–11,20,22] and chemical reduction [17]. The process involved in the coprecipitation method is operationally simple, and the commercial Ru-Zn catalyst used in Asahi-Kasei process is also prepared by this method. Liu et al. [20,22] have conducted detailed research pertaining to the preparation of Ru-Zn catalysts using the coprecipitation method and the subsequent evaluation of their catalytic activity. However, the Ru-Zn catalysts generated in these studies were coprecipitated under high alkaline conditions and washed with an alkaline solution following their preparation by the coprecipitation method, which is similar to the process used by Asahi-Kasei [8]. Using processes of this type, it can be difficult to control the Ru and Zn contents in the final Ru-Zn catalysts because Zn and even Ru atoms can be lost during the coprecipitation and washing processes under the highly alkaline conditions. Furthermore, a large amount of alkaline waste water is produced during these processes.

In this study, we have developed a new process for preparing Ru-Zn catalysts using the coprecipitation method under low alkaline conditions, whilst also avoiding the need to wash the resulting catalyst with an alkaline solution. Furthermore, the catalysts produced in this way showed high selectivity towards cyclohexene during the selective hydrogenation of benzene. The effect of the amount of $ZnCl_2$ added to the coprecipitation solution was investigated, as well as the impact of several other reaction conditions (e.g., stirring rate) and the amount of $ZnSO_4$. The stability of the optimal Ru-Zn catalyst was also evaluated.

2. Experimental

2.1. Catalyst preparation

2.1.1. Low alkaline conditions

The Ru-Zn catalysts were prepared as follows. A NaOH solution (4% (*m*/*V*), 35 mL) was quickly added into a stirred solution of $RuCl_3 \cdot xH_2O$ (2.5 g; Shenyang Nonferrous Metal Research Institute, Shenyang, China; Ru content: 36–38 wt%) and the desired amount of $ZnCl_2$ (Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) in water (250 mL), and the resulting solution was stirred for 2 h at 80 °C. The reaction mixture was then cooled to ambient temperature and stirred overnight. The supernatant (~135 g) was decanted, and the remaining mixture was placed into a 250 mL Teflon-lined autoclave. H_2 was fed into the autoclave after the system had been purged five times, and the purged mixture was reduced under 5 MPa of H_2 pressure at 150 °C and a stirring rate of 1000 r/min for 3 h. The mixture was then cooled to ambient temperature, and the resulting Ru-Zn black powder was washed with water until no Cl^- could be detected. The resulting Ru-Zn catalysts were stored in water, and a series of Ru-Zn catalysts (Ru-Zn-0 to Ru-Zn-4) was prepared by changing the amount of $ZnCl_2$ added to the coprecipitation solution. The details of these catalysts are shown in Table 1.

2.1.2. High alkalinity conditions

The Ru-Zn-5 catalyst was prepared according to the procedures from the literature [8,20,22]. Briefly, a stirred solution of $RuCl_3 \cdot xH_2O$ (2.5 g) and $ZnCl_2$ (3.25 g) in H_2O (250 mL) was treated with a NaOH solution (30% (*m*/*V*), 35 mL), and the resulting mixture was agitated for 2 h at 80 °C. The mixture was then cooled to ambient temperature to give a black precipitate, which was washed three times with a NaOH solution 4% (*m*/*V*)

Table 1
Zn contents in the Ru-Zn catalysts and their textural properties.

Catalyst	$ZnCl_2$ (g)	pH of reduction solution	Zn/Ru [a] (*m*/*m*)	Zn content [b] (wt%)	Zn/Ru [b] (*m*/*m*)	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore size [c] (nm)
Ru-Zn-0	0.00	>12	0.00	0.0	0.00	71.7	0.34	19.2
Ru-Zn-1	0.15	>11	0.08	7.6	0.10	72.8	0.32	17.0
Ru-Zn-2	0.30	~10	0.16	13.4	0.20	68.9	0.29	16.0
Ru-Zn-3	0.45	~6	0.24	16.7	0.26	58.7	0.24	17.0
Ru-Zn-4	0.60	~6	0.32	19.7	0.31	59.8	0.24	15.3
Ru-Zn-5 [d]	3.25	>13	1.73	9.6	0.13	—	—	—

[a] Theoretical value. [b] Measured by ICP. [c] BJH desorption average pore diameter (4V/A). [d] 30% NaOH aq. solution.

after the supernatant had been removed by decantation. The resulting black precipitate was dispersed in a NaOH solution (5% (*m*/*V*), 150 mL) and charged into a 250 mL Teflon-lined autoclave. The reduction process used in this particular case was similar to the method described above, except the reduction time was increased to 12 h. The reduction mixture was then cooled to ambient temperature, and the resulting Ru-Zn black powder was washed three times with a NaOH solution 5% (*m*/*V*), and then washed with water until no Cl^- could be detected. The resulting Ru-Zn catalyst was stored in water.

2.2. Catalyst characterization

The Ru-Zn catalysts prepared above were stored in water immediately after their preparation and were subsequently vacuum-dried at 40 °C prior to being characterized. The Ru and Zn contents in the catalysts were measured on an Optima 7000 DV ICP-OES Spectrometer (PerkinElmer, USA). X-ray powder diffraction (XRD) patterns were collected on an Ultima IV diffractometer (Ultima, Rigaku, Japan) using Cu K_α radiation. N_2 physisorption experiments were performed on a Micromeritics ASAP 2020 system (USA). The total surface area of each catalyst was obtained using the BET equation, and the pore size was determined by BJH desorption analysis.

Temperature-programmed reduction (TPR) experiments were performed on a PX200 Multi-sorption equipment (Tianjin Golden Eagle Technology Co., Ltd, China). In a typical run, a sample of the catalysts (without reduction) that was kept in water (~5 mg dry basis) was added with water directly to the reactor where it was heated at 300 °C for 2 h under Ar stream (10 mL/min). The H_2-TPR curves were subsequently determined by passing 5% H_2-95% Ar stream (20 mL/min) through the preheated sample whilst the temperature was increased from 25 to 500 °C at a rate of 10 °C/min. A thermal conductivity detector (TCD) was used to determine the amount of H_2 consumed by this process.

2.3. Reactivity testing

The selective hydrogenation of benzene was performed in a 250 mL autoclave (316L stainless steel or hastelloy C276, Beijing Century Senlong Experimental Apparatus Co., Ltd, China) with a magnetic stirrer. In a typical reaction, the autoclave was charged with water (70 mL), Ru-Zn catalyst (0.12 g, dry basis), $ZnSO_4\cdot7H_2O$ (8.4 g), and ZrO_2 powder (0.6 g; RC-100, Daiichi Kigenso Kagaku Kogyo Co., Ltd, Japan). H_2 gas was fed into the autoclave (1.0 MPa) immediately after it had been purged 5 times with N_2, and the autoclave was then heated at a stirring rate of 300 r/min. Benzene (35 mL) was added to the autoclave when the temperature reached 150 °C, and the H_2 pressure and the stirring rate were adjusted to 5 MPa and 1200 r/min, respectively. The reaction was then stirred at 150 °C for 10–60 min. The products in the organic phase were analyzed by GC on a GC-1690 system (Hangzhou Kexiao) equipped with an FID detector. The resulting GC data were used to calculate the benzene conversion and cyclohexene selectivity. The specific activity of the catalyst (γ_{40}) was defined as the converted amount (g) of benzene per hour over 1 g of Ru at a conversion of 40%.

For experiments concerning the recyclability of the Ru-Zn-3 catalyst, the organic phase was removed from the autoclave by suction, and the remaining slurry containing the Ru-Zn catalyst, ZrO_2, and $ZnSO_4$ was used in the next experiment. Experiments involving the recycled catalyst were conducted under the same conditions as those described above.

3. Results and discussion

3.1. Catalyst characterization results

As shown in Table 1, five unsupported Ru-Zn catalysts with different Zn contents (i.e., Ru-Zn-0 to 4) were prepared by the coprecipitation method under low alkaline conditions. The amount of the NaOH precipitant (4%) was kept constant in all of the experiments involving the addition of different amounts of $ZnCl_2$. The pH of the precipitation solution therefore decreased gradually as the amount of $ZnCl_2$ added to the mixture increased. The pH value of the reduction solution was less than 7 when the amount of $ZnCl_2$ added to the solution was greater than 0.45 g. The Ru and Zn contents in the precipitation and reduction solutions were measured by ICP, and found to be lower than 0.25 ppm in both cases, which indicated that very little Ru and Zn were lost to the solution during the precipitation and reduction processes. This result was confirmed by the similarity in the Ru/Zn ratios between the ICP results and the theoretical values.

If Ru and Zn existed in their respective atomic states in the catalysts, then the theoretical total contents of Ru and Zn in Ru-Zn-0 to 4 would be 0.91, 0.98, 1.06, 1.13, and 1.20 g, respectively. In practice, the final mass of Ru and Zn in the catalysts synthesized in the current study (i.e., Ru-Zn-0 to 4) was 0.90, 0.96, 1.11, 1.31, and 1.41 g, respectively. When the Zn content in the catalysts was higher than 16.7 wt% (e.g., Ru-Zn-3 and 4), the final mass of the catalysts was higher than the theoretical values. These results therefore suggested that these catalysts could also be made up of some Ru and Zn oxide species. Fig. 1 shows the XRD patterns of all five catalysts. When the Zn content was lower than 13.4 wt% (e.g., Ru-Zn-0 to 2), the XRD pattern only contained diffraction peaks that could be assigned to

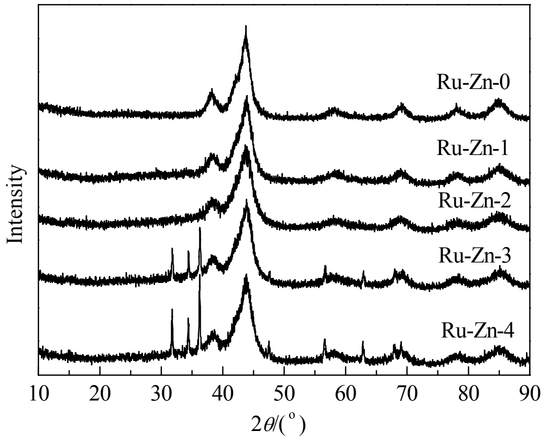

Fig. 1. XRD patterns of the Ru-Zn catalysts with different Zn contents.

the metallic Ru phase (2θ = 38.4°, 44.0°, 58.3°, 69.4°, 78.4°, and 84.7°). Evaluation of the Ru crystallite size from the XRD patterns using the Scherrer formula indicated that the nature of the Zn species had very little impact on the Ru crystallite size (~4.0 nm) in the Ru-Zn catalysts. When the Zn content was higher than 16.7 wt%, the XRD patterns contains seven diffraction peaks that could be assigned to the hexagonal phases of ZnO (2θ = 31.8°, 34.4°, 36.3°, 47.5°, 56.6°, 62.9°, and 68°), which indicated the presence of ZnO in the Ru-Zn-3 and Ru-Zn-4 catalysts. The XRD patterns of the Ru-Zn catalysts before the reduction did not contain any peaks corresponding to crystals (data not shown).

The XRD peaks corresponding to the ZnO phase were also observed for the Ru-Zn-3 catalyst after the reduction time was extended to 6 h (data not shown), which indicated that the ZnO was difficult to reduce at 150 °C under 5 MPa of H_2 pressure. These results also indicated that the ZnO particles were highly dispersed in the Ru-Zn catalysts when the Zn content was lower than 13.4 wt% (e.g., Ru-Zn-1 and Ru-Zn-2). The XRD peaks corresponding to Ru oxide were not observed for these catalysts, which indicated that they did not contain Ru oxides or the Ru oxides were highly dispersed in all of the catalysts.

To compare the properties of the Ru-Zn catalysts prepared under low alkaline conditions with those of the corresponding catalyst prepared under high alkaline conditions, we prepared Ru-Zn-5 by adding a 30% NaOH solution to the precipitation solution, and washing the resulting catalyst in NaOH aqueous solution (4% (m/V)) before reducing it in a NaOH solution (5% (m/V)). As shown in Table 1, the final Zn content of Ru-Zn-5 was only 9.6 wt% with a Zn/Ru ratio of 0.13 (as determined from the ICP data). This Zn/Ru ratio was much lower than that of the theoretical value (1.73) even though $ZnCl_2$ (3.25 g) was added to the precipitation solution. The XRD pattern of Ru-Zn-5 did not contain any diffraction peaks corresponding to the ZnO phase (data not shown), which indicated that most of the Zn species must have been lost to the solution and that it is therefore difficult to control the Zn content in Ru-Zn catalysts prepared under high alkaline conditions.

Fig. 2 shows the H_2-TPR profiles of the Ru-Zn-0 and Ru-Zn-3 catalysts without reduction. The reduction temperature for the Ru-Zn-0 catalyst was 111.3 °C, clearly much lower than that of the Ru-Zn-3 catalyst, which was 139.3 °C. This difference in the reduction temperatures of two catalysts indicated that the addition of Zn species effectively inhibited the reduction of the Ru species. The H_2-TPR profile of the Ru-Zn-3 catalyst contained a peak with shoulders between 100 and 170 °C, which were attributed to the step-by-step reduction of RuO_2 to metallic Ru [22]. Similar H_2-TPR profiles have been reported in the literature for Ru-Zn catalysts containing different Zn contents by Liu and his coworkers [22]. The temperatures required for the complete reduction of all of the Ru-Zn catalysts were close to the reaction temperature 150 °C, which indicated that metallic Ru was the only Ru species present in the catalyst when it was heated at 150 °C under 5 MPa of H_2 pressure.

The H_2-TPR profiles of the reduced Ru-Zn catalysts were also measured. The reduced Ru-Zn catalysts that had been kept in water were added directly to the H_2-TPR reactor. The samples were then dried and preheated at 300 °C in Ar gas for 2 h. The H_2-TPR profiles of the resulting materials are shown in Fig. 3. These results revealed that the reduction peak appeared at room temperature for the catalysts with low Zn contents (e.g., Ru-Zn-1 and Ru-Zn-2), and that the reduction process started from 30 °C and peaked at temperatures greater than 56 °C for the catalysts with high Zn contents (e.g., Ru-Zn-3 and Ru-Zn-4). Furthermore, the reduction peak of the catalyst with the lowest Zn content (i.e., Ru-Zn-1) was much larger than that of a catalyst with a high Zn content (e.g., Ru-Zn-3) (Fig. 4), which indicated that the catalysts with low Zn contents could be readily reduced and oxidized. In fact, the H_2-TPR reduction peaks of the catalysts reduced in the autoclave and subsequently vacuum-dried were much larger than those of the catalysts reduced in the autoclave, stored in water and directly added to the TPR reactor, especially for the catalysts with low Zn contents. Taken together, these results indicated that the reduced Ru-Zn catalysts could be readily oxidized, especially those with low Zn contents.

Interestingly, it was found that catalysts prepared with the same amount of $RuCl_3 \cdot xH_2O$ but different amounts of $ZnCl_2$ exhibited different sedimentation behavior in water. As shown in Fig. 5, the dispersion degree of the catalyst in water increased with increasing Zn content. Thus, catalysts with high Zn contents (e.g., Ru-Zn-3 and Ru-Zn-4) showed good disper-

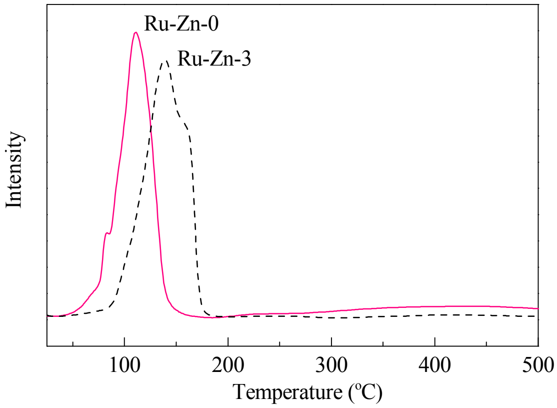

Fig. 2. H_2-TPR profiles of catalysts Ru-Zn-0 and Ru-Zn-3 before reduction.

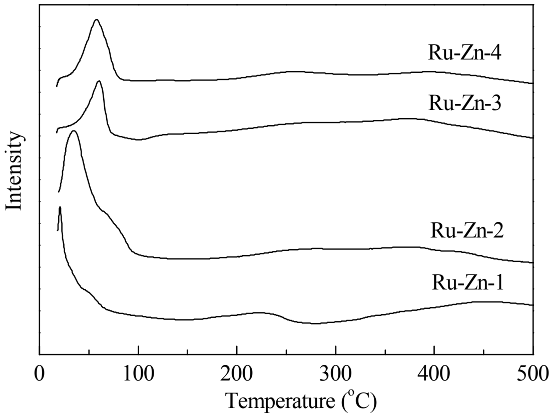

Fig. 3. H_2-TPR profiles of Ru-Zn catalysts with different Zn contents after reduction.

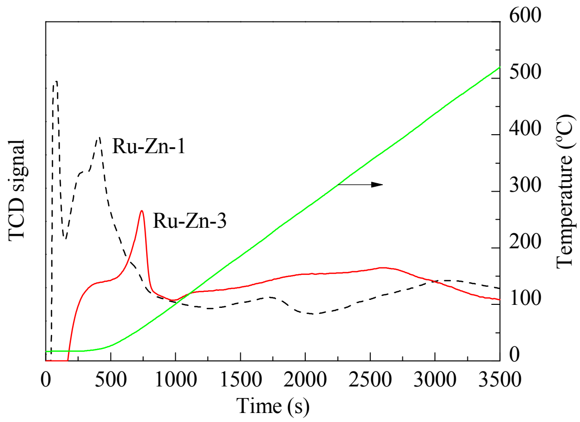

Fig. 4. H_2-TPR profiles of catalysts Ru-Zn-1 and Ru-Zn-3 after reduction.

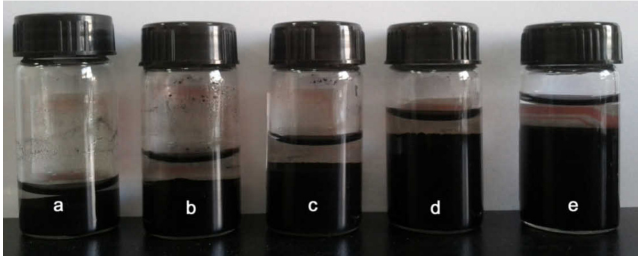

Fig. 5. Photos of Ru-Zn catalysts with different Zn contents. (a) Ru-Zn-0; (b) Ru-Zn-1; (c) Ru-Zn-2; (d) Ru-Zn-3; (e) Ru-Zn-4.

sion in water. There are three possible reasons for these differences in the dispersion behavior, including (1) the total amount of the catalyst increases with increasing Zn content; (2) the hydrophilicity of the catalyst increases with increasing Zn content; and (3) the Ru species can be readily reduced in the catalysts with low Zn contents, and the resulting catalyst can readily aggregate after reduction.

The textural properties of the Ru-Zn catalysts were characterized by N_2 physisorption, and the results are shown in Table 1. As mentioned above, the Ru-Zn catalysts were composed of Ru nanoparticles (~4 nm in diameter). The nanoparticles readily aggregated, which meant that there were mesopores in the catalysts after they had been dried. It was found that the BET surface areas and pore volumes of the catalysts with high Zn contents (e.g., Ru-Zn-3 and Ru-Zn-4) decreased significantly compared with the catalysts with low Zn contents. This result was consistent with the appearance of a ZnO phase in these two catalysts. Another reason for this decrease in the BET surface areas and pore sizes of these catalysts could be a decrease in the Ru nanoparticle contents in these catalysts. The pore sizes of catalysts containing Zn were slightly smaller than that of the catalyst without Zn. Despite these minor differences, there was no clear trend between the pore size and the Zn content in the catalysts.

3.2. Catalytic properties

3.2.1. Effects of the Zn content

The catalytic performance of the Ru-Zn catalysts with different Zn contents was investigated for the selective hydrogenation of benzene to cyclohexene. The performance of the Ru-Zn catalysts was evaluated in terms of the reaction time, benzene conversion, cyclohexene selectivity and yield, and the results are summarized in Table 2. It is noteworthy that the reaction time was adjusted according to the reactivity over the catalyst to obtain similar levels of benzene conversion. The Ru-Zn-0 catalyst, which did not contain any Zn, gave the lowest selectivity for cyclohexene over all the catalysts tested, despite also providing the lowest benzene conversion. Based on the reaction time required over the different catalysts to obtain similar levels of benzene conversion, it became clear that the activity of the catalysts decreased with increasing Zn content, whereas the selectivity and yield of cyclohexene increased. In other words, the addition of Zn led to significant improvements in the selectivity and yield of cyclohexene. As proposed in the literature [11,22], the main reason for this improvement in the selectivity and yield of cyclohexene is that the Zn component in the catalysts inhibits the resorption of the cyclohexene product onto the surface of the catalyst, and therefore suppresses the hydrogenation of cyclohexene to cyclohexane. As shown in Table 2, the Ru-Zn-0 catalyst provided lower levels of benzene conversion and cyclohexene selectivity than the Ru-Zn-1 catalyst after the same reaction time. As described above in Section 3.1, these differences in the performance of the catalysts could be attributed to the poorer dispersion of the Ru-Zn-0 catalyst in water. No significant increase was observed in the selectivity of the catalyst Ru-Zn-4 although a longer reaction time of 60 min was needed. The cyclohexene selectivity over the Ru-Zn-3 catalyst was higher than 80% with benzene conversion of 47%, and it should be possible to separate the cyclohexene and cyclohexane products by solvent extraction because of their similar boiling points. Naturally, the separation costs associated with processes with high cyclohexene selectivity will be lower than those incurred for processes with low cyclohexene selectivity. With this in mind, a cyclohexene selectivity of greater than 80% is required by the fine chemicals industry [11]. The performance characteristics of the Ru-Zn-3 catalyst clearly meet this need, indicating that the Ru-Zn-3 catalyst could potentially be used in commercial application. The Ru-Zn-3 catalyst was used to investigate the effects of several other factors on the performance of the hydrogenation reaction, and the results are discussed in detail below. According to the literature [20,22], the best Zn content for the hydrogenation of benzene to cyclohexene is 8–10 wt%. The catalysts described in those studies were prepared under highly alkaline conditions and

Table 2
Effects of the Zn content on the reaction properties.

Catalyst	Reaction time (min)	Conversion (%)	Selectivity (%)	Yield (%)
Ru-Zn-0	10	41.0	47.4	19.4
Ru-Zn-1	10	55.2	58.8	32.4
Ru-Zn-2	20	47.3	75.0	35.5
Ru-Zn-3	45	47.2	80.7	38.1
Ru-Zn-4	60	47.9	81.9	39.2
Ru-Zn-5	20	50.4	65.8	33.2

Reaction conditions: catalyst 0.12 g, ZrO_2 0.6 g, $ZnSO_4\cdot7H_2O$ 8.4 g, C_6H_6 35 mL, H_2O 70 mL, 150 °C, 5 MPa of H_2 pressure, stirring rate 1200 r/min.

had to be pretreated in the aqueous solution of $ZnSO_4\cdot 7H_2O$ and suspended ZrO_2 solution before the reaction. The Ru-Zn-3 catalyst was prepared under low alkaline conditions and did not require a pretreatment process. As shown in Table 2, the Ru-Zn-5 catalyst, which was prepared under highly alkaline conditions, showed lower selectivity as well as a lower yield of cyclohexene than the other catalysts prepared under low alkaline conditions (e.g., Ru-Zn-2 to 4). The XRD pattern of the Ru-Zn-5 catalyst did not contain any peaks that could be assigned to ZnO crystals (data no shown). Based on the results of the XRD analysis (Fig. 1) and the outcome of the reactions (Table 2), it was proposed that the presence of ZnO crystals in the Ru-based catalysts is critical to obtaining high selectivity for cyclohexene (>80%).

3.2.2. *Effects of the stirring rate*

The catalytic performance of the Ru-Zn-3 catalyst was investigated under a variety of different stirring rates, and the results are shown in Table 3. The results showed that the stirring rate had very little impact on the benzene conversion and yield of cyclohexene when it was between 1100 and 1300 r/min. Struijk et al. [13] reported a strong increase in the initial rate of hydrogen uptake with the stirring rate as the stirring rate was below 1000 r/min, and that the rate of hydrogen uptake increased only gradually at stirring rates above 1000 r/min. At stirring rates above 1000 r/min, the diffusional retardation of the reaction rate due to the mass transport of hydrogen at the gas/liquid interface and of benzene at the liquid/liquid interface is minimized. Liu's group [19] also found that the reaction selectivity for cyclohexene increased with increasing stirring rate when it was slower than 800 r/min. Struijk et al. [13] reported that stirring rates of higher than 2000 r/min led to the attrition of the catalyst, with the catalyst also adhering to the inner wall of the reactor. A stirring rate of 1400 r/min was used by Liu et al. [22] in their study of the effect of zinc contents. The results of the current study revealed that a stirring rate of 1100–1300 r/min was optimal for the production rate of cyclohexene, at least when a magnetic stirrer was used with our reactor system.

3.2.3. *Effect of the amount of $ZnSO_4$*

The zinc sulphate ($ZnSO_4\cdot 7H_2O$) concentration was varied in a series of separate experiments designed to develop a deeper understanding of the influence of salts on the performance of the Ru-Zn catalyst, and the results are shown in Fig. 6. The results show that the addition of a small amount of $ZnSO_4$ suppressed the reaction rate, but also led to a significant increase in the selectivity for cyclohexene. The initial selectivity for cyclohexene increased significantly from about 23.6% up to 89.2%, when the $ZnSO_4$ concentration was increased from 0 to 0.3 mol/L. However, a further increase in the $ZnSO_4$ concentration from 0.30 to 0.60 mol/L led to a slight decrease in the selectivity for cyclohexene although the benzene conversion and yield of cyclohexene increased significantly. Although the yield increased with increasing $ZnSO_4$ concentration, the selectivity for cyclohexene was lower than 80% when the concentration of $ZnSO_4$ was higher than 0.5 mol/L. The optimal concentration of $ZnSO_4$ was therefore determined to be 0.42–0.45 mol/L. When the concentration of $ZnSO_4$ was 0.45 mol/L, the yield of cyclohexene reached 45% with a selectivity of greater than 80%.

Table 3
Effect of stirring rate on the reaction properties over the Ru-Zn-3 catalyst.

Stirring rate (r/min)	Conversion (%)	Selectivity (%)	Yield (%)
1100	47.8	83.9	40.1
1200	48.3	82.3	39.8
1300	47.7	84.2	40.1

Reaction conditions: Ru-Zn-3 catalyst 0.12 g, ZrO_2 0.6 g, $ZnSO_4\cdot 7H_2O$ 8.4 g, C_6H_6 35 mL, H_2O 70 mL, 150 °C, 5 MPa of H_2 pressure, 45 min.

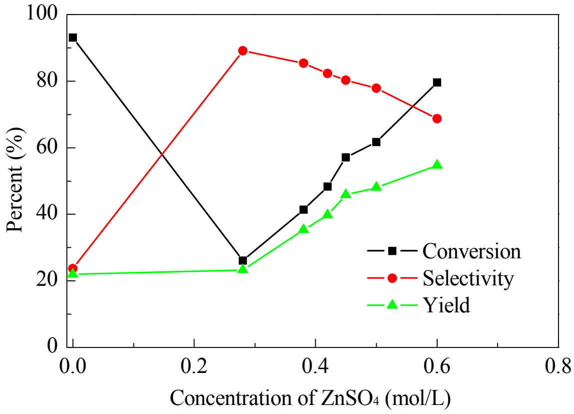

Fig. 6. Effect of the $ZnSO_4$ concentration on the outcome of the reaction. Reaction conditions: Ru-Zn-3 catalyst 0.12 g, ZrO_2 0.6 g, $ZnSO_4\cdot 7H_2O$ 0.0–12.3 g, C_6H_6 35 mL, H_2O 70 mL, 150 °C, 5 MPa of H_2 pressure, 45 min, stirring rate 1200 r/min.

The specific activity (γ_{40}) and selectivity (S_{40}) of the Ru-Zn-3 catalyst were found to be 166 g/(g·h) and 85.5% at $ZnSO_4$ concentration of 0.38 mol/L, and 185 g/(g·h) and 83.0% at $ZnSO_4$ concentration of 0.42 mol/L, respectively. Based on commercial estimations, a specific activity (γ_{40}) of greater than 100 g/(g·h) is required for the reduction of benzene to cyclohexene together with a selectivity (S_{40}) of greater than 80%, and the performance characteristics of the Ru-Zn-3 catalyst clearly meet these requirements. Furthermore, the results of the current study are comparable with data from the literature, which gave γ_{40} and S_{40} values of 155 g/(g·h) and 85.5%, respectively [34].

It has been shown that the presence of an aqueous salt solution is essential for obtaining a high yield of cyclohexene in the selective hydrogenation of benzene over Ru-based catalysts [13], and the results of the current study are similar to those reported elsewhere in the literature [14]. Liu et al. [16] investigated the influence of different Zn ion concentrations and pH values on the performance of the Ru-Fe-B/ZrO_2 catalyst, and found that the optimal concentration of Zn^{2+} in the slurry was in the range of 0.5–0.6 mol/L with a pH value of 5.4–5.5. The impact of the salt solution can be explained as follows. $ZnSO_4$ would be chemisorbed onto the surface of the Ru catalyst, which would result in the Ru becoming hydrophilic. The Ru catalyst particles would therefore be surrounded by a layer of water, which would lead to a strong diffusional resistance towards mass transfer of hydrogen and cyclohexene to the Ru surface. The presence of such a water layer would also slow

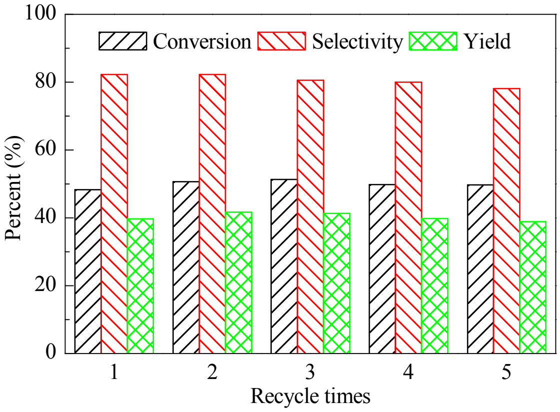

Fig. 7. Recyclability of the Ru-Zn-3 catalyst for the selective hydrogenation of benzene to cyclohexene. Reaction conditions: Ru-Zn-3 catalyst 0.12 g, ZrO_2 0.6 g, $ZnSO_4·7H_2O$ 8.4 g, C_6H_6 35 mL, H_2O 70 mL, 150 °C, 5 MPa of H_2 pressure, stirring rate 1200 r/min, 45 min.

down the hydrogenation of cyclohexene to cyclohexane because it would suppress the direct hydrogenation of the adsorbed cyclohexene. The presence of a water layer would also slow down the rate of cyclohexene re-adsorption because of the poor solubility of cyclohexene in water. Liu's group [22] recently proposed that the synergistic effect of ZnO and $ZnSO_4$ enhanced the selectivity for cyclohexene. Namely, the $(Zn(OH)_2)_3(ZnSO_4)(H_2O)_5$ salt formed by ZnO on the surface of the catalyst would react with $ZnSO_4$ and play a key role in improving the selectivity of the catalyst for cyclohexene. However, no explanation has been provided to date in the literature to account for the observed increase in the benzene conversion with increasing $ZnSO_4$ concentration. We propose that the pH value of the reaction solution decreases with increasing $ZnSO_4$ concentration, which would result in the dissolution of the ZnO on the surface of the catalyst, leading to an increase in the benzene conversion. However, further research would be required to investigate this hypothesis in detail.

3.2.4. Stability of the catalyst

The stability of the Ru-Zn-3 catalyst was investigated. The catalyst was recycled five times without the inclusion of any additives, and the results are shown in Fig. 7. The results show that the benzene conversion was stable above 48%, and that the cyclohexene selectivity and yields were kept above 76% and 40% in the first 4 recycles, respectively, which indicated that the catalyst was stable. The activity of the catalyst was slightly decreased in 5th recycle because of the inevitable loss of catalyst during the recycling process and the occurrence of 4 recycles without regeneration, however, the selectivity to cyclohexene and the yield were still as high as 78.1% and 38.9%, respectively. These results therefore show that the Ru-Zn-3 catalyst has the potential to be used in industrial application.

4. Conclusions

Unsupported Ru-Zn catalysts with different Zn contents have been successfully prepared using the coprecipitation method under low alkaline conditions. The incorporation of Zn species led to a decrease in the activity of the Ru catalyst although the selectivity was improved significantly. The optimal Zn content in the Ru-Zn catalysts was determined to be 16.7 wt% (i.e., Ru-Zn-3). The use of a stirring rate in the range of 1100 to 1300 r/min had very little impact on the catalytic reaction. The addition of small amount of $ZnSO_4$ to the reaction solution led to a decrease in the benzene conversion and a significant improvement in the selectivity, with a $ZnSO_4$ concentration of >0.3 mol/L leading to an increase in the benzene conversion. The optimal concentration of $ZnSO_4$ was found to be 0.42–0.45 mol/L. The selectivity for cyclohexene reached 80% (yield > 45%) when the conversion of benzene was 57% in $ZnSO_4·7H_2O$ solution of 0.45 mol/L under the optimal reaction conditions (i.e., hastelloy reactor, 150 °C, 5 MPa of H_2 pressure, 1200 r/min). The presence of ZnO crystals in the Ru-based catalysts was very important to obtain a high selectivity for cyclohexene (>80%). Taken together, these results demonstrate that Ru-Zn catalysts prepared under low alkaline conditions could be used for industrial application.

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Graphical Abstract

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Ru-Zn catalysts for selective hydrogenation of benzene using coprecipitation in low alkalinity

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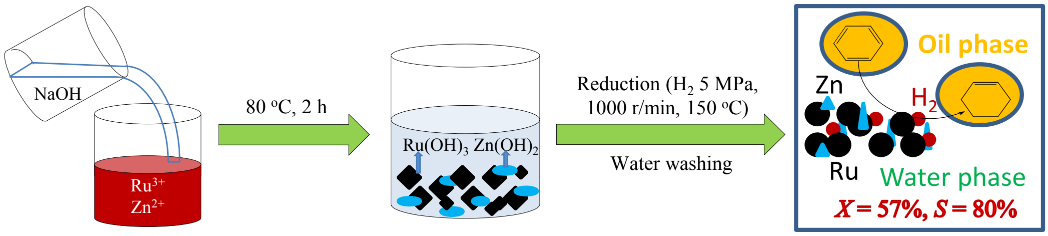

The Ru-Zn catalysts did not need to be washed after the coprecipitation and could just be washed with water (decantation) after the reduction. The Ru-Zn catalysts with a ZnO crystal phase showed high catalytic performance in the selective hydrogenation of benzene.

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