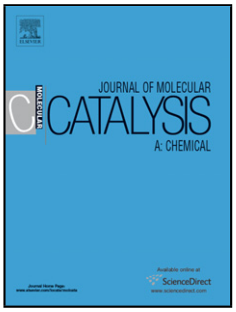

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Selective hydrogenation of benzene to cyclohexene over Ru-Zn/ZrO2 catalysts prepared by a two–step impregnation method

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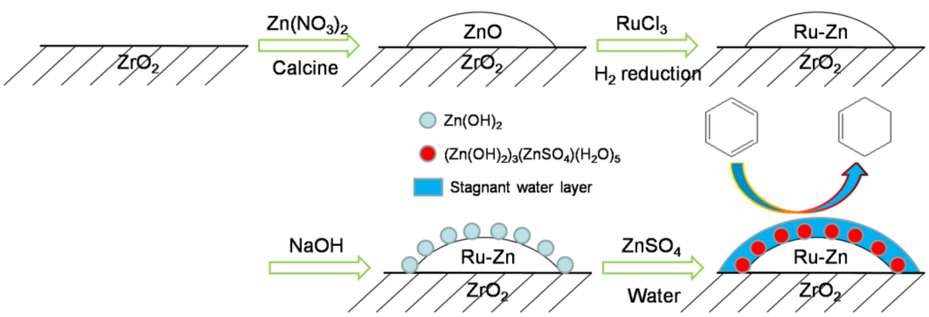
Graphical Abstract



Highlights

► Ru-Zn/ZrO_2 catalysts are prepared by two-step impregnation.

► Alkali treatment of Ru-Zn/ZrO_2 is necessary after reduction.

► Optimal composition of Ru-Zn/ZrO_2 is obtained.

► Specific activity of Ru-Zn/ZrO_2 catalysts is 4 times that of Ru-Zn catalysts.

Abstract

Supported Ru-Zn/ZrO_2 catalysts are successfully prepared by a two–step impregnation method (Zn deposition--calcination--Ru deposition), and their catalytic performances for selective liquid-phase hydrogenation of benzene are investigated. Physical properties of the catalysts are characterized by N_2 adsorption, atomic absorption spectroscopy, X-ray diffraction, temperature-programmed reduction, transmission electron micrographs, dynamic light scattering and X-ray photoelectron spectroscopy. Effects of the Zn content, concentration of alkaline treatment (NaOH) after hydrogen reduction, and hydrogen reduction temperature on the properties of Ru-Zn/ZrO_2 catalysts with a fix Ru loading of 10.0 wt% are studied. It is found that the optimal ZnO content is 10.5 wt% in the first-step impregnation (ZnO-ZrO_2), and that the alkaline treatment after hydrogen reduction is very important for obtaining the optimal Zn content in the ultimate catalyst. Over the optimal Ru-Zn/ZrO_2 catalyst with 10.0 wt% Ru and 2.78 wt% Zn, the selectivity to cyclohexene can reach 80% at the benzene conversion of 50% under the reaction condition (1200 r/min, 150 ºC, 5 MPa H_2). The specific activity of the catalyst is about 4 times higher than those of Ru-Zn catalysts prepared by coprecipitation. The recycle catalytic performance of the optimal Ru-Zn/ZrO_2 catalyst is also explored. There is no significant decrease of catalytic performance after four recycles, indicating good stability of the catalyst prepared by the two–step impregnation method.

Keywords: Two–step impregnation; Alkaline treatment; Benzene; Selective hydrogenation; Ru-Zn/ZrO_2 catalyst.

1. Introduction

Caprolactam and adipic acid are important industrial materials for production of nylon-6 and nylon-66, and they can be produced by two processes. One process includes selective oxidation of cyclohexane to cyclohexanone and cyclohexanol, and another one includes selective hydrogenation of benzene to cyclohexene. However, for selective oxidation of cyclohexane, the per-pass yield is as low as ~4% [1], and the oxidation process of cyclohexane is prone to explosion. In contrast, the selective hydrogenation of benzene usually affords higher per-pass yield (~40%), and the process is safer. Cyclohexene, as an intermediate product in the hydrogenation of benzene, is a thermodynamically less favorable product. To obtain cyclohexene with high selectivity, the reaction should be carried out in a tetraphase reaction system (gas (hydrogen), oil (benzene), water and solid (catalyst)), and the catalyst with high performance is needed.

There are many research reports about the selective hydrogenation of benzene [2–6]. Preparation of effective catalysts taking both activity and selectivity into consideration is critical to this reaction. To date, ruthenium is widely accepted as the most effective metal for selective hydrogenation of benzene to cyclohexene, and many different metals as promoters are reported [7–23]. Ruthenium catalysts for selective hydrogenation of benzene can be divided into two major types: unsupported Ru nanoparticles [24–30] and supported Ru catalysts [7–23,31–33]. The latter is highly desirable because the noble metal has high dispersion on the support surface and shows high activity. The Ru-Zn catalyst prepared by the coprecipitation method has been used in the commercial plant with the disperser of ZrO_2 by Asahi-Kasei Corporation. Therefore, Ru-Zn supported ZrO_2 catalysts have been extensively investigated.

Fan et al. [31] prepared Ru-Zn/*m*-ZrO_2 catalysts by coprecipitation of $RuCl_3$ and $ZrOCl_2$ with $NH_3 \cdot H_2O$, followed by hydrogen reduction of the product in an $ZnSO_4$ aqueous solution (0.14 M) at 180 ^oC for 40 min under 4.28 MPa H_2 pressure. The highest cyclohexene yield over Ru-Zn/*m*-ZrO_2 catalysts was 43.4% (conversion 69.3% and selectivity 62.7%), and the specific activity was 994 gBenzene/(gRu·h). Yuan et al. [9,10] prepared Ru-Zn/ZrO_2 catalysts by coprecipitation of $RuCl_3$ and $ZrOCl_2$ with KOH followed by reduction in different concentration $ZnSO_4$ solution at 180 ^oC for 8 h, under 5.0 MPa H_2 pressure, and obtained the catalysts with the Zn content of 2.42~2.95 wt%. The best cyclohexene yield up to 44% was obtained at the Zn content of 2.72 wt%. Huang and Liu [32] prepared Ru-Zn/ZrO_2 catalysts by coprecipitation of $RuCl_3$, $ZnSO_4$ and ZrO_2 with NaOH and reduction in the autoclave at 150 ^oC and 1000 r/min for 3 h under 5.0 MPa H_2 pressure. The highest cyclohexene yield up to 41.2% (conversion 68.5% and selectivity 60.1%) was obtained. Han et al. [23] prepared Ru/ZnO-$ZrO_x(OH)_y$ catalysts by coprecipitating a certain amount of ZnO, $ZrO(NO_3)_2$ and $RuCl_3$ in the solution of NaOH and $NaBH_4$, and reducing the obtained solid in a hydrogen flow at 180 ^oC for 2 h. The Ru loading in the catalysts was 3 wt%. When the Zn/Zr molar ratio was 10:1, the highest cyclohexene yield was 56.0% (conversion 77.5% and selectivity 72.3%), and the specific activity was 258 gBenzene/(gRu·h).

Ru-M-B/ZrO_2 catalysts were prepared using a chemical reduction method (also called reduction-impregnation method) and the effects of transition metals (M=La, Cr, Mn, Fe, Co, Ni, Cu, and Zn) on the catalytic performance of the catalysts were investigated by Liu et al. [17,18,33]. It was found that the Ru-Co-B/ZrO_2 catalyst exhibited excellent selectivity for cyclohexene (82.8% at the conversion of 75.8%) and good stability, indicating its good prospect for industrial applications. The specific activity of the Ru-Co-B/ZrO_2 catalyst was 448 gBenzene/(gRu·h).

Many Ru supported catalysts with other hydrophilic supports (SiO_2 [7,8], γ-Al_2O_3 [20], SBA-15 [11,12,16], Nb_2O_5 [13], TiO_2 [14] and hydroxyapatite (HAP) [15]) have also been investigated. For example, the Ru-Ce/SBA-15 catalyst exhibited a maximum cyclohexene yield of 53.8% at the $ZnSO_4$ concentration of 0.42 M in the reactor [12]. The bimetallic Ru-Zn catalysts supported on HAP with different Ru/Zn molar ratios were prepared by the ion-exchange method [15]. The yield of cyclohexene can reach 33.0% (conversion 69.8%, selectivity 47.3%) over Ru-Zn/HAP with a Ru/Zn molar ratio of 1:1 and Ru loading of 2.5 wt% at 150 °C and 5 MPa of hydrogen. Overall, the catalytic performances of Ru supported SiO_2, γ-Al_2O_3, Nb_2O_5 catalysts were lower than that of Ru supported ZrO_2 catalysts.

Although Ru supported catalysts have been extensively investigated, only unsupported Ru-Zn catalysts with dispersant of zirconia are being used in industrial plants. The Ru-Zn supported ZrO_2 (Ru-Zn/ZrO_2) catalyst should be a good candidate for commercial utilization because it has similar properties with the unsupported Ru-Zn catalyst dispersed in ZrO_2 aqueous suspension. Based on commercial estimations, a selectivity of greater than 80% is required for the selective hydrogenation of benzene to cyclohexene at the conversion of 50%. However, the selectivity of many Ru-Zn/ZrO_2 catalysts reported in the literature was lower than 80% at the benzene conversion of 50%. In this study, we demonstrate that Ru-Zn/ZrO_2 catalysts can be prepared by a two–step impregnation method with further treatment in an alkaline solution, which show a high selectivity to cyclohexene (>80% at the conversion of 50%) and high activity in the selective hydrogenation of benzene. Effects of the $Zn(NO_3)_2{\cdot}6H_2O$ amount in the first-step impregnation, concentration of NaOH for alkaline treatment of catalysts after hydrogen reduction, and hydrogen reduction temperature are investigated. Finally, the stability of the optimal $Ru\text{-}Zn/ZrO_2$ catalyst is evaluated.

2. Experimental

2.1. Materials

$RuCl_3{\cdot}xH_2O$ (Kunming Sino-platinum Metals Co., Ltd, Ru≥37%), ZrO_2 powder (RC-100, Daiichi Kigenso Kagaku Kogyo Co., Ltd., Japan), $ZnSO_4{\cdot}7H_2O$ (Wako Pure Chemical Industries, Ltd.). Other chemicals including $Zn(NO_3)_2{\cdot}6H_2O$, NaOH and benzene were purchased from Sinopharm Chemical Reagent Co., Ltd. Deionized water was used in all experimental processes.

2.2. Catalyst preparation

Ru-Zn/ZrO_2 catalysts were prepared by a two–step impregnation method, and the detailed procedure is as follows.

(1) Preparation of ZnO-ZrO_2 supports with various ZnO contents

Introduction of Zn species was achieved through the impregnation method. A desired amount of $Zn(NO_3)_2{\bullet}6H_2O$ was dissolved in 3 mL deionized water in a glass beaker, then 2.25 g ZrO_2 powder was added and stirred for 1 h. The glass beaker was sealed with plastic wrap and placed at 60 ^oC in a convection oven for 2 h, then the sample was left to dry off at 100 ^oC after removing the plastic wrap. The obtained solid was transferred to a tube furnace for calcination at 250 ^oC for 1 h, and 300^oC for 1 h at the air flow of 20 mL/min. The resulting ZnO-ZrO_2 samples with various ZnO contents in ascending order were denoted as ZnO-ZrO_2-n (n=0-5) and the detailed amount of $Zn(NO_3)_2 \cdot 6H_2O$ is listed in Table 1.

(2) Preparation of Ru-Zn/ZrO_2 with various Zn contents

Introduction of Ru species was also achieved through the impregnation method. 0.60 g $RuCl_3 \cdot xH_2O$ was dissolved in 3 mL water, and the obtained ZnO-ZrO_2 support (2.00 g) was added to the $RuCl_3 \cdot xH_2O$ solution in a beaker. After stirred for 2 h, the beaker was sealed with plastic wrap and placed at 60 ^oC in an oven for 1 h. Then the sample was left to dry off in a water bath at 90 ^oC without the plastic wrap, and transferred to a tube furnace for gas reduction in a hydrogen flow of 30 mL/min at a certain temperature (typically 200^oC) for 3 h. The reduction product was treated with 100 mL of NaOH aqueous solution (typically 0.01 M) for 3 times, and then washed with 100 mL of deionized water for 7 times until no Cl^- ions were detected. The catalysts with different Zn contents were kept in water and their solid contents were determined, which were denoted as Ru-Zn/ZrO_2-n (n=0-5) (Table 2).

2.3. Catalyst characterization

The obtained Ru-Zn/ZrO_2 catalysts kept in water were vacuum-dried at 60 ^oC prior to characterization. Zinc contents were measured by the atomic absorption spectroscopy (AAS). X-ray powder diffraction (XRD) patterns were collected on an Ultima IV diffractometer (Rigaku, Japan) using Cu Kα radiation. N_2 physisorption was performed on a Micromeritics ASAP 2020 equipment at 77 K, and the sample was heated at 423 K under vacuum for 2 h before measurement. The total surface area was obtained by the

BET equation and the pore size was determined by BJH desorption. Dynamic light scattering (DLS) was performed with Malvern ZEN 3600 to detect the particle size distribution of catalysts. Surface analysis of the catalysts was analyzed by X-ray photoelectron spectroscopy (XPS) on a PHI Quantera SXM instrument using a monochromatized Al Kα radiation (E_b=1486.6 eV) at an energy resolution of 0.5 eV and at a base pressure of 3×10^{-8} Pa.

The surface morphology and particle sizes were measured by transmission electron microscopy (TEM) on a Tecnai G2 F30 microscope operated at 200 kV. The catalysts were dispersed in anhydrous ethanol, sonicated for 10 min, and dropped onto a carbon-film-coated copper grid. Particle-size-distribution histograms were obtained by randomly measuring at least 100 nanoparticles.

The temperature-programmed reduction (TPR) was performed on a PX200 Multi-sorption equipment (Tianjin Golden Eagle Technology Co., Ltd.). The sample of $ZnO-ZrO_2$ after impregnation of $RuCl_3$ without reduction (~30 mg dry base) was directly installed into the reactor and pretreated at 200 ºC for 2 h under Ar (20 mL/min). The H_2-TPR curve was determined by passing a stream of 5% H_2 in Ar (20 mL/min) through the pretreated samples and the temperature was increased from 30 ºC to 500 ºC at a linearly programmed rate of 5 ºC/min. A thermal conductivity detector (TCD) was used to measure the amount of H_2 consumed.

2.4. Reactivity testing

The selective hydrogenation of benzene was performed in a hastelloy autoclave (250 mL) equipped with a magnetic stirrer. In a typical experiment, water (70 mL),

$ZnSO_4·7H_2O$ (8.4 g) and catalyst (0.3 g, dry base) were put into the autoclave; after being purged by hydrogen (2 MPa) five times to remove the air, the autoclave was heated with a stirring rate of 300 r/min. When the temperature was increased to 150 ºC, benzene (35 mL) was introduced into the autoclave, and the H_2 pressure and the stirring rate were adjusted to 5 MPa and 1200 r/min, respectively. For the catalysts with different Zn contents, the reaction was carried out at 150 ºC for different periods to obtain the conversion of ca. 40% and 50%. The products were analyzed using a gas chromatography (Hangzhou Kexiao) with a flame ionization detector (FID). The benzene conversion and cyclohexene selectivity were calculated by the GC result. The S_{50} is defined as the selectivity of cyclohexene at the conversion of 50%. The specific activity of the catalyst (g/g·h) is defined as the converted benzene amount (g) per hour for 1 g Ru, and the γ_{50} is the specific activity at the conversion of 50%.

For the recycle activity measurement of Ru-Zn/ZrO_2-3 catalyst, the organic phase was removed from the autoclave by suction and the remaining catalyst slurry containing the Ru-Zn/ZrO_2 catalyst and $ZnSO_4$ was used for next activity evaluation. The recycle activity measurement was the same with the above procedure but the catalyst amount was 0.9 g instead of 0.3 g.

3. Results and discussion

3.1. Catalyst characterization

As shown in Table 1, six ZnO-ZrO_2 supports with different Zn contents, ZnO-ZrO_2-0 to ZnO-ZrO_2-5, were prepared by impregnation method and calcined at 250 ^oC for 1 h, and 300 ^oC for 1 h. The amount of ZrO_2 (2.25 g) was kept constant when the

$Zn(NO_3)_2 \cdot 6H_2O$ adding amount was varied. Fig. 1 shows the XRD patterns of the $ZnO-ZrO_2$ supports with different Zn contents ($ZnO-ZrO_2$-0 to $ZnO-ZrO_2$-5). When the $Zn(NO_3)_2 \cdot 6H_2O$ adding amount is lower than 0.97 g ($ZnO-ZrO_2$-0 to $ZnO-ZrO_2$-2), there are only diffraction peaks assigned to monoclinic phase of ZrO_2 (JCPDS: 00-024-1165). When the $Zn(NO_3)_2 \cdot 6H_2O$ adding amount is $\geq$ 0.97 g, a diffraction peak at 2θ of 36.3^o (Other peaks are covered by the peaks from ZrO_2.) ascribed to the hexagonal phases of ZnO (JCPDS: 01-070-2551) indicates the existence of ZnO crystals in the $ZnO-ZrO_2$-3 to $ZnO-ZrO_2$-5 supports. Evaluation of the ZnO crystallite size from XRD using the Scherrer formula indicates that the ZnO crystallite sizes are 45.7 nm, 46.7 nm and 43.6 nm, respectively. For the $ZnO-ZrO_2$-1 and $ZnO-ZrO_2$-2, there is no peak at 2θ of 36.3^o, indicating that the ZnO species are highly dispersed in these two supports [34].

The XRD patterns of six $Ru-Zn/ZrO_2$ catalysts with different Zn contents, $Ru-Zn/ZrO_2$-0 to $Ru-Zn/ZrO_2$-5, are shown in Fig. 2. These catalysts have the same Ru content of 10 wt%. Compared with Fig. 1, there are no peaks at 2θ of 36.3^o in Fig. 2a, indicating that the ZnO crystals vanished away in the second impregnation and washing steps. It can also be confirmed by measuring the Zn content using AAS (Table 2). The measured Zn content is much lower than the incorporated amount. Because $RuCl_3$ solution is acidic (pH 1~2), some ZnO crystals will be dissolved into $ZnCl_2$, and the dissolved Zn species will be washed away during washing process using alkaline solution and water. It makes their measured Zn contents lower than the incorporated amounts (Table 2). A weak diffraction peak at 2θ of 44.0^o assigned to the metallic Ru phase (JCPDS: 01-070-0274) can be observed in Fig. 2a. To have a better characterization, we achieved XRD patterns by slow scan of 0.5 ^{o}/min between 38^o and 48^o, and subtracted

XRD patterns of ZrO_2 from each to gain particular XRD patterns (Fig. 2b). Evaluation of Ru crystal sizes from XRD patterns (Fig. 2b) using the Scherrer formula showed that Ru crystal sizes were 4.2 nm, 4.8 nm, 4.6 nm, 5.1 nm, 4.8 nm and 4.6 nm, respectively. This indicates that there are no significant differences for the Ru crystal size in Ru-Zn/ZrO_2 catalysts with different Zn contents.

Fig. 3 shows the H_2-TPR profiles of six Ru-Zn/ZrO_2 catalyst precursors (without reduction). For the Ru-Zn/ZrO_2-0 catalyst precursor without Zn, there is a wide reduction peak at 112 ^{o}C, whereas the main reduction peak is at 160-204 ^{o}C for other catalyst precursors. According to the literature [35-37], unsupported $RuCl_3$ is reduced at lower temperature (~142 ^{o}C) and supported Ru oxide at higher temperature (160-205 ^{o}C). Therefore, we deduce that the peak of 112 ^{o}C is attributed to the reduction of $RuCl_3$ species. The reduction temperature of $RuCl_3$ in the ZnO-ZrO_2-0 catalyst precursor is lower than the literature value. This is probably due to the highly dispersed $RuCl_3$ in the ZnO-ZrO_2-0 catalyst precursor. As the $RuCl_3$ solution is acidic in the process of impregnation, some ZnO particles were dissolved into $ZnCl_2$, and $RuCl_3$ hydrolysed into $Ru(OH)_3$ and then dehydrated into Ru_xO_y during drying for catalyst precursors Ru-Zn/ZrO_2-1 to Ru-Zn/ZrO_2-5. Therefore, the reduction peaks of catalyst precursors Ru-Zn/ZrO_2-1 to Ru-Zn/ZrO_2-5 are near 160-204 ^{o}C (Fig. 3), attributed to the reduction of $Ru(OH)_3$ or Ru_xO_y. The reduction peak temperature increased from 160 ^{o}C to 175 ^{o}C with the increase of Zn content in the catalysts (Ru-Zn/ZrO_2-1 to Ru-Zn/ZrO_2-3), whereas the reduction peak temperature is higher than 185 ^{o}C (even 204 ^{o}C) for the catalysts Ru-Zn/ZrO_2-4 and Ru-Zn/ZrO_2-5. This indicates that the interaction between Ru species and Zn species increases with the increase of Zn content. When the incorporated

Zn content is as high as 10.9 wt% and 16.5 wt% in the catalysts Ru-Zn/ZrO_2-4 and Ru-Zn/ZrO_2-5, respectively, the high content of Zn species results in the smaller BET specific surface area, pore volume and pore size of the ZnO-ZrO_2 support as shown in Table 1. It is difficult to obtain high dispersion of Ru species in the support with smaller pore volume and pore size, resulting in a very high reduction peak temperature.

3.2. Catalytic properties

3.2.1. Effects of Zn content

The catalytic performance of Ru-Zn/ZrO_2 catalysts with different Zn contents for selective hydrogenation of benzene to cyclohexene was investigated. The reaction time, benzene conversion, cyclohexene selectivity and yield over the Ru-Zn/ZrO_2 catalysts are summarized in Table 3. In order to obtain a benzene conversion around 40~50%, the reaction time was adjusted according to the activity of the catalyst. The selectivity (S_{50}) and specific activity (γ_{50}) were calculated from two different experimental points. From the specific activity or γ_{50} value, it is known that the incorporation of Zn species into the catalyst decreased the activity of the catalyst. At the same benzene conversion, the activity of the catalysts decreased (e.g., γ_{50}), and the selectivity of cyclohexene (e.g., S_{50}) increased with increasing the Zn content from the catalyst ZnO-ZrO_2-0 to the catalyst ZnO-ZrO_2-3, whereas the selectivity decreased with increasing the Zn content from ZnO-ZrO_2-3 to ZnO-ZrO_2-5.

For the first three catalysts (Ru-Zn/ZrO_2-1 to Ru-Zn/ZrO_2-3), the addition of Zn can significantly improve the selectivity and yield of cyclohexene. As proposed in the literature [25], the main reason is considered to be that the zinc component inhibits the resorption of cyclohexene generated on the catalyst surface to suppress hydrogenation of cyclohexene to cyclohexane. However, when the Zn content further increased from Ru-Zn/ZrO_2-3 to Ru-Zn/ZrO_2-5, the selectivity of cyclohexene declined. That is, the catalyst Ru-Zn/ZrO_2-3 showed the highest selectivity and yield of cyclohexene. As discussed in section 3.1, the much higher reduction peak temperature of catalysts Ru-Zn/ZrO_2-4 and Ru-Zn/ ZrO_2-5 than that of other catalysts (Ru-Zn/ZrO_2-1 to Ru-Zn/ZrO_2-3) indicates the bigger particle size of Ru species in catalysts Ru-Zn/ZrO_2-4 and Ru-Zn/ ZrO_2-5. That is, some of Ru crystals (relatively large Ru particles) with less Zn species around them existed in the Ru-Zn/ZrO_2 catalysts with too high Zn species, resulting in the decrease of the cyclohexene selectivity of catalysts Ru-Zn/ZrO_2-4 and Ru-Zn/ZrO_2-5. The XRD patterns of ZnO-ZrO_2 (Fig. 1) showed that ZnO crystals (40~50 nm) became increasingly accumulated from ZnO-ZrO_2-4 to ZnO-ZrO_2-5, whereas the ZnO particles highly dispersed without ZnO diffraction peaks for ZnO-ZrO_2-1 and ZnO-ZrO_2-2. The accumulation of ZnO particles may lead to the decrease of Zn species around Ru species, resulting in the decrease of the selectivity of the catalyst.

Under the optimal conditions, the selectivity to cyclohexene is higher than 80% at the benzene conversion of 50% over the Ru-Zn/ZrO_2-3 catalyst. In industrial process, the reaction products of benzene, cyclohexene and cyclohexane should be separated by solvent extraction due to their close boiling point. The higher the selectivity to cyclohexene is, the cheaper the cost of separation is. Therefore, the cyclohexene selectivity of more than 80% is requested by industry. Obviously, the performance of Ru-Zn/ZrO_2-3 catalyst meets this need. That is, the Ru-Zn/ZrO_2-3 catalyst showed a potential in commercial application. It is worth mentioning that the most common unsupported catalysts for selective hydrogenation of benzene to cyclohexene were prepared by coprecipitation and the value of γ_{50} was usually about 100~200 gBenzene/(gRu·h) [29,30] at the conversion of 50%, but here the value of γ_{50} for the Ru-Zn/ZrO_2-3 catalyst can reach higher than 800 gBenzene/(gRu·h). This is the big superiority for the supported Ru-Zn/ZrO_2 catalysts prepared by the two–step impregnation method as compared with the unsupported Ru-Zn catalysts prepared by the coprecipitation method.

To have a better comparison with the two–step impregnation method, we also prepared a catalyst (Ru-Zn/ZrO_2-3a) by a one–step impregnation method, that is, the same amount $Zn(NO_3)\cdot 6H_2O$ and $RuCl_3\cdot xH_2O$ as Ru-Zn/ZrO_2-3 were simultaneously dissolved in 3 mL water, and then impregnated with 2.25 g ZrO_2. The hydrogen reduction and alkaline treatment were the same as the two–step impregnation method. The catalytic performance of the catalyst (Ru-Zn/ZrO_2-3a) was also shown in Table 3. The selectivity is 57.8% at the conversion of 56.8%, which is much lower than that of Ru-Zn/ZrO_2-3 prepared by the two–step impregnation method. This indicates that the two–step impregnation method is very important for the preparation of supported Ru-Zn/ZrO_2 catalysts with high catalytic performance.

3.2.2. Effects of NaOH concentration

After hydrogen reduction of the Ru-Zn/ZrO_2 catalysts, they were treated 3 times with 100 mL NaOH (0.01 M) and washed 7 times with 100 mL deionized water. In order to further elucidate the performance principle of the Ru-Zn/ZrO_2 catalysts prepared by our method, the effects of NaOH concentration were investigated. The results are shown in

Table 4. With increasing the NaOH concentration from 0.0 to 0.01 M, S_{50} enhanced from 77.1% to 81.6%, and γ_{50} decreased by 42%. With increasing the NaOH concentration from 0.01 to 0.025 M, S_{50} enhanced lightly and γ_{50} decreased by 24%. In other words, the increase degree of S_{50} decreased with the further increase of NaOH concentration from 0.01 to 0.025 M. The Zn content was 0.05, 2.78 and 3.48 wt%, respectively, when the NaOH concentration was 0.00, 0.01 and 0.025 M. We measured the pH of the solution for the first 3 times washings with water when the NaOH concentration was 0.00 M and found that the pH was about 3.5 for all 3 times. This is because $RuCl_3$ solution is acidic (pH 1~2) in the process of impregnation, and part of ZnO will dissolve into $ZnCl_2$; therefore, the sample was also weak acidic after hydrogen reduction. Zn species in the catalyst would be dissolved in acidic solutions; therefore, the Zn content measured was as low as 0.05 wt%. When treated 3 times with 0.01 M NaOH, the measured pH of the filtrate solution was about 6.5, 11.5 and 12.0, respectively, while treated 3 times with 0.025 M NaOH, the measured pH value was about 6.5, 12.0 and 12.5, respectively. Mixing the filtrate solutions of 3 times treatments, white precipitate of $Zn(OH)_2$ in the solution was observed, indicating that part zinc species were in the filtration solution. Because the pH values of filtration solutions from three alkaline treatments were all higher than 6.0, some Zn species could be fixed in the solid catalyst as $Zn(OH)_2$ or ZnO. The higher the treating NaOH concentration, the more Zn species remained in the solid catalyst. Therefore, the Zn content increased with the increase of the NaOH concentration. The catalyst activity decreases with the increase of the Zn content. Therefore, the γ_{50} value decreased with increasing the NaOH concentration of alkaline treatment.

To the best of our knowledge, this is the first time to use the alkaline treatment process after the hydrogen reduction of the supported Ru catalyst solid particles in the impregnation method. The two–step impregnation method was used to prepare Ru-Zn supported catalysts on SiO_2, SiO_2-Al_2O_3, SiO_2-ZrO_2 by Liu et al. [38], however, the alkaline treatment was not employed and the catalysts were reduced at very high temperature (e.g., 400 ^oC). The selectivity to cyclohexene of those catalysts was just around 40% at the conversion of 30-50%.

XPS spectra of O 1s region peak fitting for lattice oxygen (530 eV) and oxygen in surface hydroxyl (532 eV) [39] for the catalysts washed with water (a) and treated with 0.01 M NaOH (b) are shown in Fig. 4. There is a large amount of surface hydroxyl groups in monoclinic ZrO_2 itself, and we found that oxygen of surface hydroxyl in the catalyst treated with the NaOH solution (Fig. 4b) was more than that in the catalyst washed with water (Fig. 4a). This indicates that the Zn species existed in the form of $Zn(OH)_2$ for the catalyst treated with NaOH.

Qiao et al. [40] prepared Ru-Zn/ZrO_2 catalysts using a deposition-precipitation method, and the reduced Ru-Zn/ZrO_2 catalysts in solution were then subjected to alkaline post-treatment by using NaOH aqueous solution (5-30 wt%) for five times. They concluded that upon treatment with NaOH solutions, dealloying of the binary Ru-Zn/ZrO_2 catalysts occurred, resulting in Ru/ZrO_2 catalysts with smaller Ru nanoparticles. The concentration of 5-30 wt% is equal to 1.25-7.5 M, which is much higher than the concentration used in this study (e.g. 0.01 M). The Zn species was almost completely dissolved out after alkaline treatment in the case of ref. 40. The alkaline treatment in this study was used to neutralize the acidity of the catalyst precursors. Therefore, with respect to this function, the alkaline treatment in this study is different from ref. 40. It is also concluded in ref. 40 that alkaline post-treatment was able to introduce more hydroxyl groups on the catalyst surface, rendering improved hydrophilicity. This is consistent with our above result that oxygen of surface hydroxyl in the catalyst treated with the NaOH solution was more than that in the catalyst washed with water. The increase of hydrophilicity of the catalysts improved their selectivities in benzene selective hydrogenation.

Recently, Liu and coworkers [25] proposed that the synergistic effect of ZnO and $ZnSO_4$ enhances the selectivity to cyclohexene. Namely, the $(Zn(OH)_2)_3(ZnSO_4)(H_2O)_5$ salt formed by the reaction of ZnO on the catalyst surface with $ZnSO_4$ plays a key role in improving the selectivity to cyclohexene of the catalyst. Based on the above results, we proposed a schematic plot of Ru-Zn/ZrO_2 catalysts for benzene selective hydrogenation as shown in Fig. 5. Herein, we proposed that the $(Zn(OH)_2)_3(ZnSO_4)(H_2O)_5$ salt formed during the reaction in the autoclave from $Zn(OH)_2$ instead of ZnO. Due to tremendous solubility difference between benzene and cyclohexene in water, the stagnant water layer formed by $(Zn(OH)_2)_3(ZnSO_4)(H_2O)_5$ causes a strong diffusion resistance for cyclohexene to the ruthenium surface as compared with benzene. That is, the presence of the stagnant water layer slows down the further hydrogenation of cyclohexene to cyclohexane due to the suppression of the direct hydrogenation of adsorbed cyclohexene. This makes the decline of catalyst activity and the increase of selectivity to cyclohexene with the increase of $Zn(OH)_2$ by enhancing NaOH concentration for alkaline treatment after hydrogen reduction.

3.2.3. Effects of reduction temperature

The preparation of Ru-Zn/ZrO_2-3 catalyst under different reduction temperatures was investigated and the results are shown in Table 5. It can be seen that the benzene conversion and yield of cyclohexene significantly changed when the reduction temperature increased from 150 ^{o}C to 250 ^{o}C. That is, the catalyst activity decreased when the reduction temperature increased, whereas the selectivity of cyclohexene got an optimal value at the reduction temperature of 200 ^{o}C. For the reduction temperature of 250 ^{o}C, the catalyst activity is very low. As mentioned in the introduction section, most Ru-Zn/ZrO_2 catalysts were reduced at 150-180 ^{o}C [9,10,23,31,32].

To investigate the reason of low activity of the catalyst reduced at 250 ^{o}C, we achieved XRD patterns of the three catalysts by slow scan of 0.5 ^{o}/min between 38^{o} and 48^{o}, and subtracted XRD pattern of ZrO_2 from each to gain particular XRD patterns (Fig. 6). Evaluation of Ru crystal sizes from XRD using the Scherrer formula indicates that Ru crystal sizes are 4.3, 5.1 and 4.8 nm, respectively. As shown in Fig. 7, TEM images and particle-size-distribution histograms with Gaussian analysis fittings of the Ru particles (Fig. 7) in the catalysts with different reduction temperatures (150 ^{o}C, 200 ^{o}C and 250 ^{o}C) indicate that Ru crystal sizes are 3.71, 3.80 and 4.66 nm, respectively. This means that the Ru crystallite size in Ru-Zn/ZrO_2 catalysts slightly increased with the increase of reduction temperature. This is probably one of the reasons for the lower activity of the catalysts reduced at higher temperature.

As shown in Table 5, the Zn content of the catalyst increased with the increase of reduction temperature, that is, the measured values of Zn content were 1.34 wt%, 2.78 wt% and 3.57 wt%, respectively. The higher Zn content will decrease the catalyst activity, therefore, this might be one reason for the lower activity of catalysts reduced at higher temperatures. From the increase of Zn content in the catalyst, we guess the interaction between Ru species and Zn species also increased with the reduction temperature. The strong interaction may also decrease the catalytic activity.

We measured the size distributions of catalysts obtained from different reduction temperatures by DLS (Fig. 8), and average secondary particle sizes are 574.3 nm, 638.1 nm and 933.1 nm, respectively; in other words, the average secondary particle size increased by 1.46 times when the reduction temperature increased from 200 ^{o}C to 250 ^{o}C. This is probably one of the reasons for the sharp activity decrease of catalysts reduced at 250 ^{o}C as compared with that reduced at 200 ^{o}C, because the dispersion of catalyst in water is very important to the tetraphase catalytic reaction system.

3.2.4. Stability of the catalyst

The stability of Ru-Zn/ZrO$_2$-3 (2.78 wt% Zn, 10.0 wt% Ru) catalyst was investigated. The catalyst was recycled four times without any addition after every reaction, and the results are shown in Fig. 9. As can be seen, the benzene conversions were stable above 53%, and the cyclohexene selectivity and yields were kept above 78% and 42% in the four recycles, respectively, indicating a good stability of the catalyst. The benzene conversion was 54.6%, and the cyclohexene selectivity and yields was 80.1% and 43.8% in the first recycle, and slightly decreased in the 4th recycle after three recycles without regeneration. However, the benzene conversion, the selectivity to cyclohexene and the yield were still as high as 54.3%, 78.4% and 42.4%, respectively. The specific activity was sustained at about 740 g/(g·h) when the catalyst amount was 0.9 g. Thus Ru-Zn/ZrO$_2$-3 catalyst has good prospect for industrial application.

4. Conclusions

Supported Ru-Zn/ZrO_2 catalysts with different Zn contents were successfully prepared by a two–step impregnation method and alkaline treatment after reduction. The incorporation of zinc species can decrease the activity of the ruthenium catalyst, whereas the highest selectivity can be obtained at an optimal Zn content. The optimal ZnO content in ZnO-ZrO_2 support is 10.5 wt% for Ru-Zn/ZrO_2 catalysts with Ru content of 10.0 wt% (i.e., Ru-Zn/ZrO_2-3), and the final Zn content in the catalyst is 2.78 wt%. We obtained the optimal S_{50} up to 81.6% and the specific activity (γ_{50}) > 800 g/(g·h), four times higher than unsupported Ru-Zn catalysts preparation by coprecipitation method. Alkaline treatment of the catalysts after hydrogen reduction with 0.01 M NaOH aqueous solution significantly decreased the catalyst activity and increased the selectivity of cyclohexene as compared with just washing the catalyst with water, and further increasing the NaOH concentration could only improve the selectivity to cyclohexene slightly. The reduction temperature showed significant effect on the catalytic properties of the catalyst, and the optimal reduction temperature is 200 ^{o}C. The cost of the catalyst for selective hydrogenation of benzene is expected to decrease, implying good prospect for industrial application.

Acknowledgements

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Figure Captions

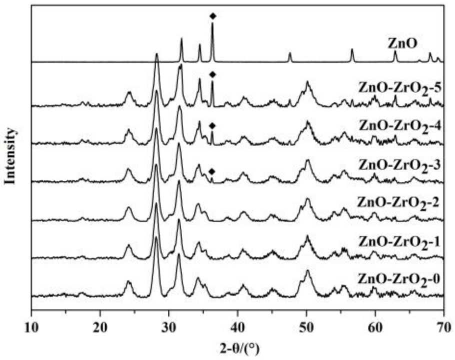

Fig. 1. XRD patterns of ZnO-ZrO_2 samples with different Zn contents.

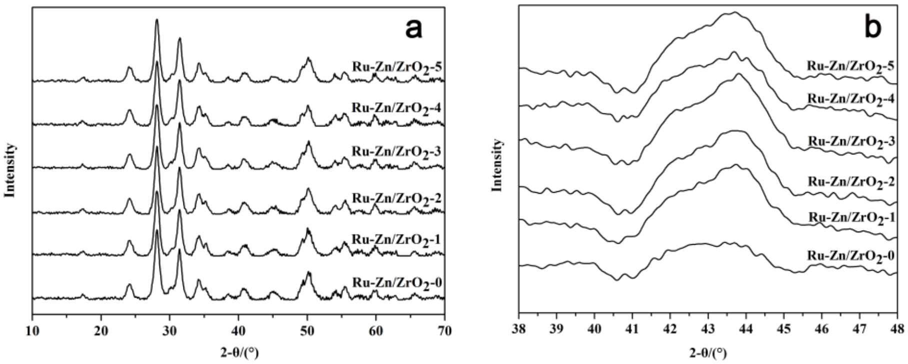

Fig. 2. XRD patterns of Ru-Zn/ZrO_2 catalysts with different Zn contents. (b) XRD patterns of ZrO_2 were subtracted from data in (a).

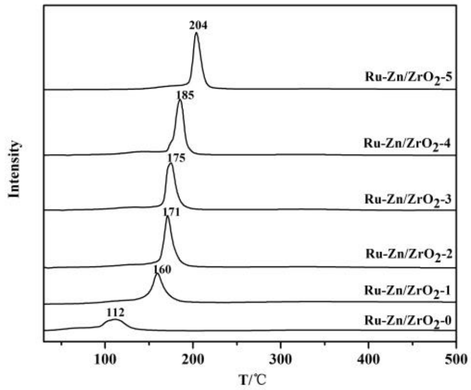

Fig. 3. H_2-TPR profiles of Ru-Zn/ZrO_2 catalysts before reduction, (b) is minizone of (a).

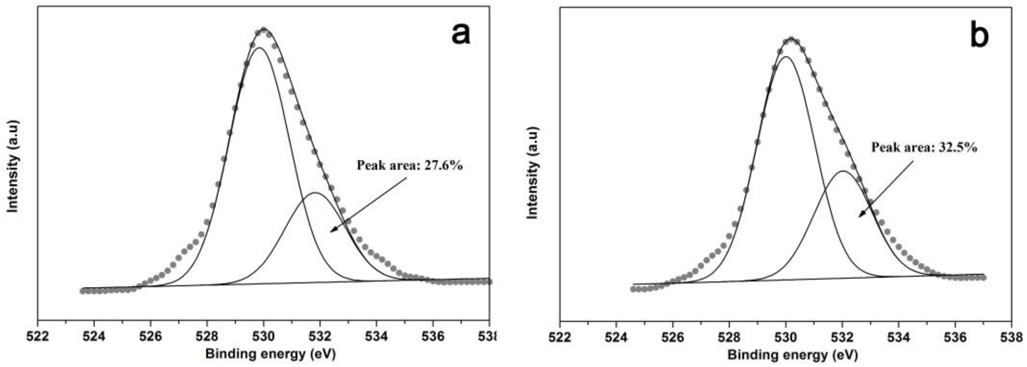

Fig. 4. XPS spectra of O 1s for catalysts (a) washed with water, (b) treated with 0.01 M NaOH.

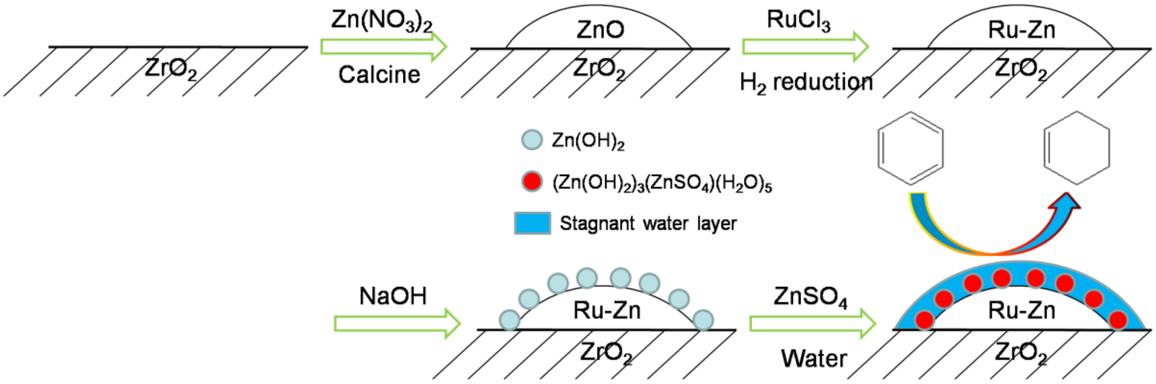

Fig. 5. Schematic diagram of formation of the Ru-Zn/ZrO$_2$ catalyst and its catalytic performance.

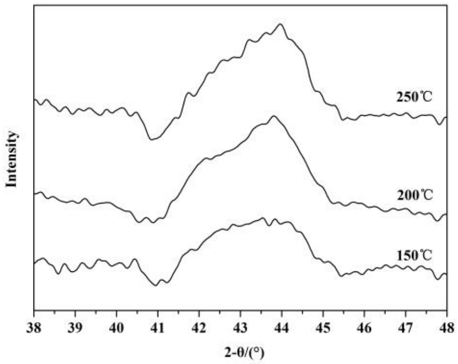

Fig. 6. XRD patterns of Ru-Zn/ZrO_2-3 catalysts with different reduction temperatures.

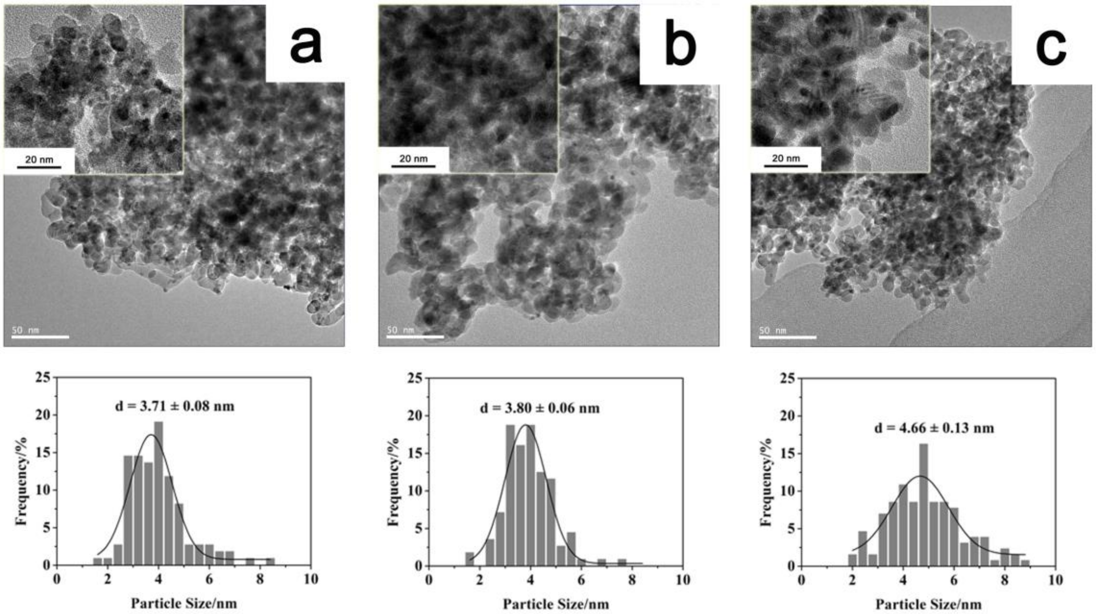

Fig. 7. TEM images and particle-size-distribution histograms with Gaussian analysis fittings of the Ru particles in catalysts with different reduction temperatures (a) 150^{o}C, (b) 200^{o}C and (c) 250^{o}C.

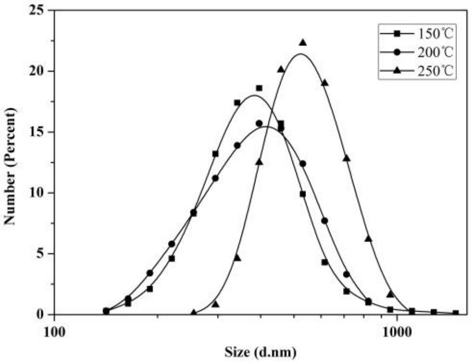

Fig. 8. DLS patterns of size distribution of Ru-Zn/ZrO_2-3 catalysts with different reduction temperatures.

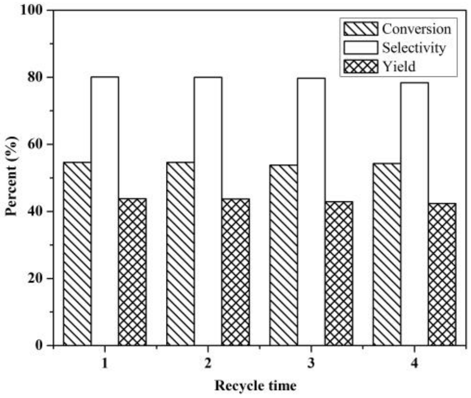

Fig. 9. Recycle of the Ru-Zn/ZrO$_2$-3 catalyst for selective hydrogenation of benzene to cyclohexene. Reaction conditions: Ru-Zn/ZrO$_2$-3 catalyst 0.9 g, ZnSO4·7H$_2$O 8.4 g, C_6H_6 35 mL, H_2O 70 mL, H_2 5 MPa, stirring rate 1200 r/min, 150 ºC, 15 min.

Tables

Table 1. Textural properties of ZnO-ZrO_2 supports with different ZnO contents.

Support	$Zn(NO_3)_2 \cdot 6H_2O$[a] (g)	ZnO Content (wt%)	BET (m^2/g)	Pore volume (cm^3/g)	Pore size[b] (nm)
ZnO-ZrO_2-0	0.00	0.0	95.2	0.32	9.5
ZnO-ZrO_2-1	0.49	5.6	89.6	0.28	9.2
ZnO-ZrO_2-2	0.73	8.1	-	-	-
ZnO-ZrO_2-3	0.97	10.5	84.5	0.25	8.8
ZnO-ZrO_2-4	1.46	15.0	73.6	0.22	8.4
ZnO-ZrO_2-5	2.43	22.7	68.1	0.20	8.4

[a] The amount of ZrO_2 is 2.25 g; [b] BJH desorption average pore diameter (4V/A).

Table 2. Textural properties of Ru-Zn/ZrO_2 catalysts with different Zn contents.

Catalyst	Incorporated Zn amount (wt%)	Zn loading[a] (wt%)	BET (m^2/g)	Pore volume (cm^3/g)	Pore size[b] (nm)
Ru-Zn/ZrO_2-0	0.0	0.00	90.3	0.23	8.1
Ru-Zn/ZrO_2-1	4.1	1.75	86.6	0.21	9.0
Ru-Zn/ZrO_2-2	5.9	2.25	-	-	-
Ru-Zn/ZrO_2-3	7.6	2.78	93.2	0.22	7.8
Ru-Zn/ZrO_2-4	10.9	3.80	92.2	0.23	8.2
Ru-Zn/ZrO_2-5	16.5	5.50	93.4	0.25	8.9

[a] Measured by AAS; [b] BJH desorption average pore diameter (4V/A).

Table 3. Effects of the Zn content on the reaction properties of catalysts[a].

Catalyst	Reaction time (min)	Conversion (%)	Selectivity (%)	Yield (%)	Specific activity (g/g·h)	γ_{50} (g/g·h)	S_{50} (%)
Ru-Zn/ZrO_2-0	5	39.6	66.3	26.2	4863		
Ru-Zn/ZrO_2-1	21	39.1	80.9	31.6	1143	1047	76.5
	30	50.8	76.2	38.7	1040		
Ru-Zn/ZrO_2-2	24	38.9	81.5	31.7	995	955	78.2
	33	51.1	77.9	39.8	951		
Ru-Zn/ZrO_2-3	26	37.8	85.1	32.1	893	867	81.6
	37	52.0	81.0	42.1	863		
Ru-Zn/ZrO_2-4	31	41.3	81.2	33.6	818	797	78.7
	42	53.9	77.6	41.8	788		
Ru-Zn/ZrO_2-5	43	29.8	80.2	23.9	426		
Ru-Zn/ZrO_2-3a[b]	40	56.8	57.8	32.8	872		

[a] Reaction condition: catalyst 0.3 g, $ZnSO_4·7H_2O$ 8.4 g, C_6H_6 35 mL, H_2O 70 mL, H_2 5 MPa, stirring rate 1200 r/min, 150 ºC; [b] Prepared by one–step impregnation method.

Table 4. Effects of the NaOH concentration for alkaline treatment on reaction properties of catalyst Ru-Zn/ZrO_2-3[a].

c_{NaOH} (M)	Zn loading (wt%)[b]	Reaction time (min)	Conversion (%)	Selectivity (%)	Yield (%)	Specific activity (g/g·h)	S_{50} (%)	γ_{50} (g/g·h)
0.00	0.05	13	38.3	80.3	30.7	1809	77.1	1709
		23	60.6	74.3	45.0	1618		
0.01	2.78	26	37.8	85.1	32.1	893	81.6	867
		37	52.0	81.0	42.1	863		
0.025	3.48	40	43.6	84.1	36.6	669	82.3	653
		60	61.1	79.3	48.5	625		

[a] Reaction condition: catalyst 0.3 g, $ZnSO_4 \cdot 7H_2O$ 8.4 g, C_6H_6 35 mL, H_2O 70 mL, H_2 5 MPa, stirring rate 1200 r/min, 150 ºC; [b] Measured by AAS, the incorporated value is 7.6 wt%.

Table 5. Effects of reduction temperature on catalytic properties of catalyst Ru-Zn/ZrO_2-3[a].

Reduction Temperature (°C)	Zn loading (wt%)[b]	Reaction time (min)	Conversion (%)	Selectivity (%)	Yield (%)	Specific activity (g/g·h)
150	1.34	11	42.3	68.0	28.8	2361
200	2.78	30	43.3	82.9	35.9	886
250	3.57	150	41.8	76.5	32.0	171

[a] Reaction conditions: Ru-Zn/ZrO_2-3 catalyst 0.3 g, $ZnSO_4·7H_2O$ 8.4 g, C_6H_6 35 mL, H_2O: 70 mL, H_2 5 MPa, 150 ºC; [b] Measured by AAS, the incorporated amount is 7.6 wt%.