



# Partial hydrogenation of benzene over the metallic Zn modified Ru-based catalyst

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## ABSTRACT

From the adsorption point of view, partial hydrogenation of benzene to cyclohexene over the metallic Zn modified Ru-based catalyst was experimentally and theoretically investigated. A decreased hydrogenation activity but increased selectivity to cyclohexene over the prepared Ru-Zn/ZrO<sub>2</sub> catalyst was observed in the partial hydrogenation of benzene. Theoretical calculations suggest that the above phenomena are mainly resulted from the depression of the chemisorption of benzene and cyclohexene on the modified catalyst, especially for the latter. Undesired deep hydrogenation from cyclohexene to cyclohexane in the middle and late reaction stage therefore is effectively retarded, by which an improved cyclohexene yield is guaranteed. An optimal Zn content of 2.72 wt.% in the Ru-based catalyst was proposed by both the experiment and calculation for the partial hydrogenation of benzene, and a cyclohexene yield up to 44% was obtained over Ru-Zn/ZrO<sub>2</sub> catalyst.

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## 1. Introduction

Partial hydrogenation of benzene, which is first industrialized by Asahi Chemical Industry Co. in 1989, is of vital importance to the environmentally benign production of caprolactam. Compared with the traditional hydrogenation processes, Asahi technology features some unique characteristics as follows: the hydrogenation is applied in a tetra-phase reaction system; the hydrophilic Ru-based catalyst is suspended in a water phase containing a large amount of ZnSO<sub>4</sub> [1–4]. The presence of the water phase effectively blocks the re-adsorption of cyclohexene from the organic phase onto the catalyst surface since the solubility of cyclohexene in the water phase is only 1/17 that of benzene at the reaction temperature of 418 K. ZnSO<sub>4</sub> dissolved in the water phase is considered to serve a dual purpose. First, direct hydrogenation from benzene to cyclohexane is prohibited because of the adsorption of Zn<sup>2+</sup> at the most active sites. Second, the hydrophilicity of the catalyst surface is improved in the presence of Zn<sup>2+</sup>, which is unfavorable for the adsorption of cyclohexene [5].

Numerous efforts were devoted to the development of novel catalysts for this system, and now researchers have come to some agreements in this field.

- The active component of the catalysts is limited to the Ru metal. Extremely poor cyclohexene yield once was reported over the Ni membrane and nylon supported Pt, which means the adsorption

behavior or surface reaction mechanism of the involved species over the Ru metal should be widely different from that over other group VIII metals [6–9].

- Non-porous supports, e.g. ZrO<sub>2</sub>, TiO<sub>2</sub> and SiO<sub>2</sub>, are preferentially adopted to avoid deep hydrogenation of cyclohexene during the pore diffusion [10,11].
- Measures to improve the hydrophilicity of the catalyst, such as the adsorption of organic additives, are advantageous to the selectivity to cyclohexene [12,13].

The latest work focused on the surface modification of the Ru-based catalysts. Liu et al. developed amorphous alloy catalysts Ru-M-B/ZrO<sub>2</sub> (M = La, Fe) and a cyclohexene yield as high as 53.2% was observed over Ru-La-B/ZrO<sub>2</sub> [14,15]. La<sup>3+</sup> or in metallic state was supposed to stabilize the amorphous alloy structure and improve the activity and selectivity of the catalysts. By reducing the precursor in the ZnSO<sub>4</sub> contained water phase, Fan et al. introduced metallic Zn into the Ru-based catalyst and obtained a 43% cyclohexene yield over the prepared Ru-Zn/ZrO<sub>2</sub> [16]. Detailed roles of metallic Zn in the catalytic system were not explicitly explained. Recently, Qiao et al. prepared Ru-M/SBA-15 catalysts (M = Sn, Fe, Ba, Ce) by a “two solvents” impregnation method [17,18]. A satisfied cyclohexene yield up to 53.8% was reported over Ru-Ce/SBA-15. The beneficial effect of the Ce promoter on the selectivity to cyclohexene was ascribed to the enhancement of the hydrophilicity of the catalyst and to the electron transfer between the Ce(III) species and metallic Ru.

By the reported cyclohexene yield, Ru-Zn/ZrO<sub>2</sub> surely is not the most distinguished one among the above mentioned catalysts. However, investigation on its performance concerns a common

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problem in the partial hydrogenation of benzene; that is, the adsorbed  $\text{Zn}^{2+}$  ions can be reduced since the reaction between the  $\text{Zn}^{2+}$  ion and the adsorbed H atom has a negative reaction enthalpy [16]. In other words, the presence of metallic Zn in the bulk phase or on the surface of the Ru-based catalyst is just a general phenomenon no matter it is introduced during the reduction treatment of the precursor or during the partial hydrogenation of benzene.

Considering the reaction pathway of heterogeneous catalysis, the authors propose that the chemisorption of benzene and cyclohexene as well as their sequential hydrogenation kinetics should be affected by the presence of metallic Zn in the Ru-based catalyst. On the basis of the authors' previous work, chemisorption and hydrogenation kinetics of cyclohexene on the metallic Zn modified Ru-based catalyst are both seriously depressed [19]. In order to present a comprehensive understanding to the roles of metallic Zn in the Ru-based catalysts, in this work partial hydrogenation of benzene over Ru-Zn/ZrO<sub>2</sub> was further studied from the adsorption point of view with the combination of the surface characterization, hydrogenation experiment and theoretical calculation.

## 2. Theoretical and experimental methods

### 2.1. Experimental procedures

#### 2.1.1. Preparation and evaluation of the Ru-Zn/ZrO<sub>2</sub> catalyst

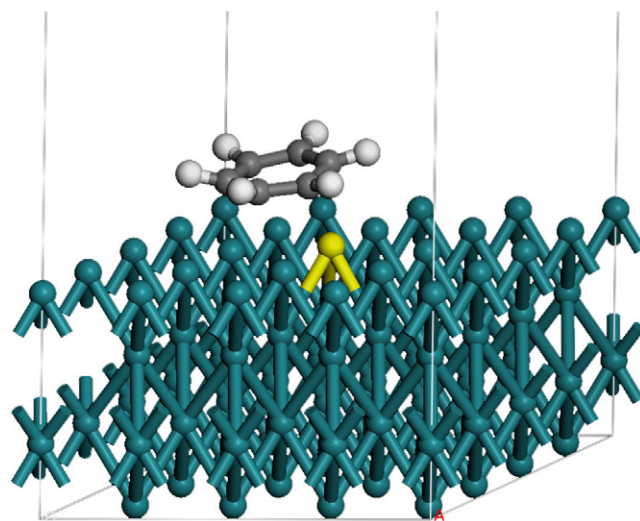
**2.1.1.1. Preparation of the precursor.** The catalyst was prepared by the coprecipitation method. At ambient temperature and under vigorous agitation, 60 ml  $\text{ZrOCl}_2$  solution of 0.2 M was added dropwise into a three-neck flask containing 100 ml KOH solution of 0.2 M within 2 min. The suspension was then heated and thermostated at 353 K. After that, 150 ml  $\text{RuCl}_3$  solution of 0.025 M was added into the suspension at a flow rate of 3 ml/min. The obtained precipitation was aged at ambient temperature overnight, followed by centrifugal wash with deionized water till no chlorine ions were detected.

**2.1.1.2. Reduction of the precursor.** The precursor, a certain amount of  $\text{ZnSO}_4$ , 150 ml deionized water and 80 ml benzene were loaded into an autoclave with a capacity of 500 ml. This autoclave also was used in the subsequent hydrogenation. After sealing and purging with low pressure  $\text{H}_2$  several times, the reduction was carried out at a temperature of 453 K and  $P_{\text{H}_2}$  of 5.0 MPa for 8 h to ensure a thorough reduction of active components.

**2.1.1.3. Evaluation of the catalyst.** In each run, a certain amount of  $\text{ZnSO}_4$ , 2.0 g catalyst, 80 ml benzene and 150 ml deionized water were loaded into the autoclave. Then, the hydrogenation was carried out at 418 K and  $P_{\text{H}_2}$  of 5.0 MPa, the fluctuation of the reaction temperature and pressure being controlled within  $\pm 0.5$  K and  $\pm 0.1$  MPa, respectively. A stirring rate of 1500 rpm was adopted to eliminate the effect of external diffusion on the hydrogenation kinetics. Organic phase was sampled at a fixed time interval of 10 min, the obtained samples being analyzed on a HP6890 gas chromatograph equipped with a PEG 20,000 capillary column.

#### 2.1.2. Characterization of the catalyst

Before characterization, the Ru-Zn/ZrO<sub>2</sub> catalyst was treated by centrifugal wash with deionized water in order to remove the adsorbed  $\text{Zn}^{2+}$ . Valence state of the elements on the catalyst surface was analyzed on a Kratos Axis Ultra DLD X-ray photoelectron spectrograph. Powder X-ray diffraction patterns of the catalysts were detected on a Bruker D8 advance X-ray diffractometer using Ni-filtered  $\text{Cu K}\alpha$  radiation. The tube voltage was 40 kV and the current was 40 mA. The composition analysis of the catalysts was performed on an IRIS Intrepid inductively coupled plasma instrument.



**Fig. 1.** Schematic of a benzene molecule adsorbed on a  $4 \times 4$  four-layer Ru-Zn/Ru(0001) slab; surface concentration of Zn atoms: 1/16; green balls represent Ru atoms and the yellow one Zn atom. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

### 2.2. Theoretical background

The ruthenium metal has a hexagonal crystal structure. In this work, it was found that metallic Zn in the Ru-Zn/ZrO<sub>2</sub> catalyst exists mainly on the surface of the Ru microcrystal to form a Ru-Zn alloy. Therefore, theoretical calculations on the adsorption of benzene and cyclohexene were based on the closest packing plane of the Ru metal, i.e. (0001) surface, and on the Ru-Zn/Ru(0001) surface alloy to simulation the adsorption occurred on the traditional Ru-based and Ru-Zn alloy catalyst, respectively. The Ru-Zn/Ru(0001) surface alloy was constructed by replacing the Ru atom with the Zn atom on the upmost layer of the Ru(0001) surface.

The calculations were performed with the Vienna ab initio Simulation Package (VASP). This program performs periodic calculations based on the density functional theory (DFT) with a plane-wave basis set. The projector-augmented wave (PAW) method and the generalized gradient approximation (GGA) level with the functional of PW91 were used. A cutoff of 400 eV was applied to the plane-wave basis set, which allowed convergence to 0.01 eV in the total energy. All structures were optimized until the forces on all unconstrained atoms were less than 0.01 eV/Å.

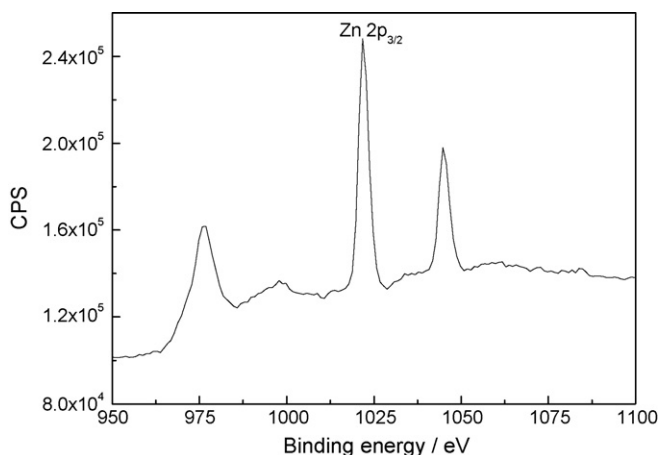
The Ru(0001) surface and Ru-Zn/Ru(0001) surface alloy were modeled by a periodic  $4 \times 4$  four-layer slab, the latter containing a single Zn atom on its first layer, refer to Fig. 1. The top two layers of the four substrate layers were allowed to relax, together with the adsorbate layer. The bottom two layers were kept fixed in bulk positions to represent the semi-infinite bulk crystal beneath the surface. A vacuum space of 15 Å was applied to separate the central slab and its periodic images.

The Brillouin-zone integrations were performed on a 3-3-1 Monkhorst-Pack grid in accordance with the size of the slab. In the preliminary calculations, smearing values of 0.1 and 0.2 eV were simultaneously attempted to improve the SCF convergence. No obvious difference in the optimized geometries was found, and the difference in the calculated heats of adsorption was less than 4%. A smearing width of 0.2 eV thereby was adopted in the subsequent calculations.

The heat of adsorption ( $\Delta H$ ) is given by

$$\Delta H = E_{\text{Adsorption}} - E_{\text{Slab}} - E_{\text{Molecule}} \quad (1)$$

where  $E_{\text{Slab}}$  and  $E_{\text{Molecule}}$  are the total energies of the relaxed bare slab and of the free adsorbate molecule, respectively, while



**Fig. 2.** XPS spectrum of Ru-Zn/ZrO<sub>2</sub> catalyst reduced in the water phase containing ZnSO<sub>4</sub> of 0.55 M.

$E_{\text{Adsorption}}$  represents the total energy of the relaxed surface/adsorbate adsorption system.

The variation of work function ( $\Delta\Phi$ ) of the catalyst surface due to the adsorbate adsorption is defined as

$$\Delta\Phi = \Phi_{\text{Adsorption}} - \Phi_{\text{Slab}} \quad (2)$$

where  $\Phi_{\text{Adsorption}}$  and  $\Phi_{\text{Slab}}$  are the work function of the relaxed surface/adsorbate adsorption system and of the relaxed bare slab, respectively.

### 3. Results and discussion

#### 3.1. Characterization of the prepared catalyst

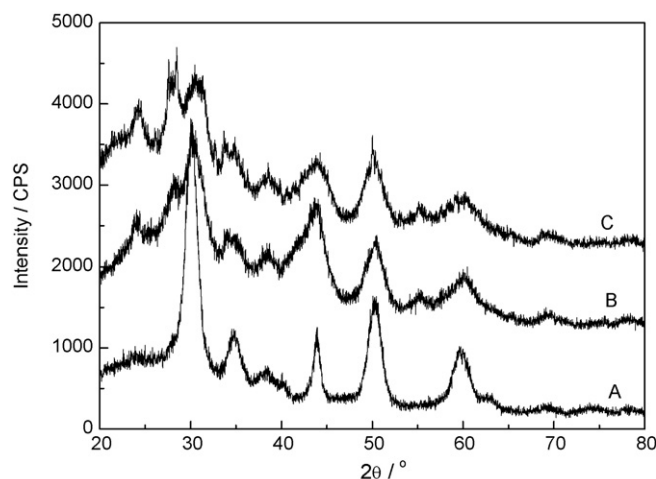
First, XPS characterization was applied to the prepared Ru-Zn/ZrO<sub>2</sub> catalysts. A  $2p_{3/2}$  peak of Zn element appears on the observed spectra at the binding energy of 1021.8 eV; refer to Fig. 2. It is confirmed that Zn element presented in the Ru-Zn/ZrO<sub>2</sub> catalysts is in the metallic state by reason that the corresponding binding energies of  $2p_{3/2}$  orbital of Zn<sup>2+</sup>, ZnO and Zn are located at 1023.1, 1022.5 and 1021.8 eV, respectively [20–22].

Subsequent ICP analysis showed that Zn content in the Ru-Zn/ZrO<sub>2</sub> could be adjusted by changing Zn<sup>2+</sup> concentration in the water phase during the reduction treatment of the precursor. As the data listed in Table 1 suggest, Zn content in the catalyst increases from 2.42 to 2.95 wt.% along with the elevation of Zn<sup>2+</sup> concentration from 0.35 to 0.55 M. A saturated Zn content surely exists since further elevation of Zn<sup>2+</sup> in the water phase has little influence on the metallic Zn content in the prepared catalyst.

XRD characterization detected diffraction peaks of the support ZrO<sub>2</sub> at  $2\theta$  values of 30.2°, 50.2° and 59.7°; refer to Fig. 3. According to Scherrer equation, the average size of ZrO<sub>2</sub> particles is all smaller than 5 nm, which means the catalysts are in the nano-scale. Besides, diffraction peaks of hexagonal Ru with broadened tendency were also found at  $2\theta$  values of 38.7°, 43.9° and 69.3°, indicating that the Ru metal supported on ZrO<sub>2</sub> is in the form of microcrystal. Although the previous XPS analysis confirmed the existence of metallic Zn in the catalyst, no corresponding diffraction peaks of the Zn metal were detected. In other words, metallic Zn should be highly dis-

**Table 1**  
Effect of Zn<sup>2+</sup> concentration in the water phase on the Zn content of the prepared Ru-Zn/ZrO<sub>2</sub> catalyst.

Zn <sup>2+</sup> concentration (M)	0.35	0.45	0.55
Zn content of the catalyst (wt.%)	2.42	2.72	2.95

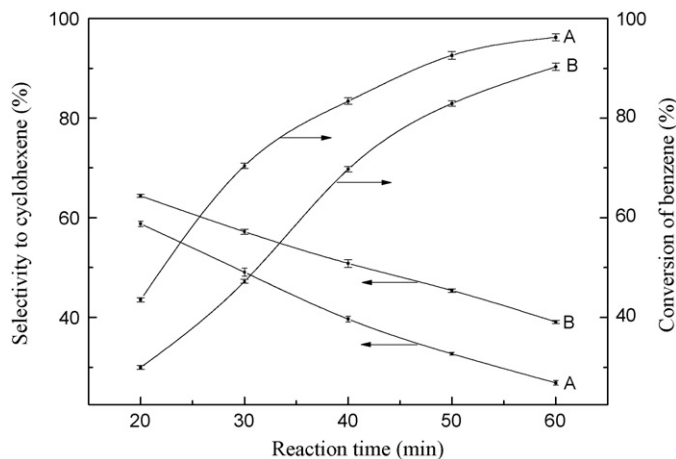


**Fig. 3.** Effect of Zn<sup>2+</sup> concentration in the water phase on the crystal pattern of the prepared Ru-Zn/ZrO<sub>2</sub> catalyst; Zn<sup>2+</sup> concentration: (A) 0.00 M, (B) 0.35 M, and (C) 0.55 M.

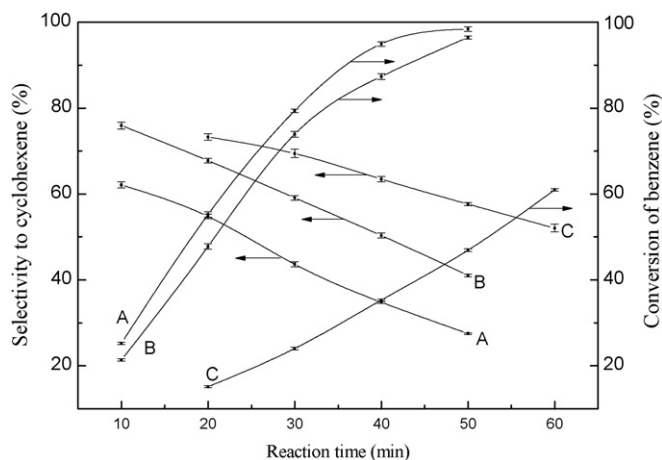
persed in the catalyst. By the considerations that Zn<sup>2+</sup> can only be reduced by the H atoms adsorbed on the Ru crystal and no evident bias of diffraction pattern of hexagonal Ru occurs along with the elevation of the Zn content in the alloy catalyst, metallic Zn should mainly exist on the surface of Ru microcrystal rather than entering its bulk phase. A Ru-Zn/Ru(0001) surface alloy, which was supposed to be a reasonable approximation to the supported Ru-Zn alloy catalyst, thus was adopted in the subsequent theoretical calculations.

#### 3.2. Partial hydrogenation of benzene over Ru-Zn/ZrO<sub>2</sub> catalyst

On the basis of the reaction pathway of heterogeneous catalysis, it is deduced that the presence of metallic Zn as well as its surface concentration in the Ru-based catalyst should exert influence on the adsorption of benzene and cyclohexene. Eventually, the hydrogenation behavior of the involved species over the modified catalyst would be affected. By adjusting Zn content in the catalyst, the above deduction was experimentally verified in the partial hydrogenation of benzene over Ru-Zn/ZrO<sub>2</sub> at two levels of Zn<sup>2+</sup> concentration in the water phase, i.e. 0.45 and 0.55 M, with the results presented in Figs. 4 and 5.



**Fig. 4.** Effect of Zn content in the Ru-Zn/ZrO<sub>2</sub> catalyst on the partial hydrogenation of benzene; Zn<sup>2+</sup> concentration in the water phase: 0.45 M; Zn content in the catalyst: (A) 2.42 wt.% and (B) 2.72 wt.%.



**Fig. 5.** Effect of Zn content in the Ru-Zn/ZrO<sub>2</sub> catalyst on the partial hydrogenation of benzene; Zn<sup>2+</sup> concentration in the water phase: 0.55 M; Zn content in the catalyst: (A) 2.42 wt.% and (B) 2.72 wt.%, C 2.95 wt.%.

The experimental data indicate a complicated synergetic effect between metallic Zn and the adsorbed Zn<sup>2+</sup> ions on the partial hydrogenation behavior of benzene. In the absence of Zn<sup>2+</sup> in the water phase, a sole usage of the modified catalyst only leads to an extremely poor cyclohexene yield. At the same time, the reaction is out of control because of too high hydrogenation rate. Nevertheless, two tendencies are clearly presented as follows: at a fixed concentration of Zn<sup>2+</sup> in the water phase, an increase in the Zn content in the modified catalyst results in a monotonously decreased catalytic activity but an improved selectivity to cyclohexene.

As the experimental data presented in Figs. 4 and 5 suggest, variation of Zn content in the alloy catalyst has a totally different influence on the catalytic activity and on the selectivity to cyclohexene. Seeing that the yield of cyclohexene is determined simultaneously by the conversion of benzene and by the selectivity to cyclohexene, an optimal Zn content in the Ru-Zn/ZrO<sub>2</sub> catalyst therefore should exist. At the Zn<sup>2+</sup> concentration of 0.55 M, a satisfied cyclohexene yield of 44% was observed over Ru-Zn/ZrO<sub>2</sub> with the Zn content of 2.72 wt.%. Further elevation of Zn content to 2.95 wt.% resulted in a sharp decrease in the catalytic activity, while the residence time to obtain the highest cyclohexene yield was excessively extended.

### 3.3. Adsorption of benzene and cyclohexene on the Ru(0001) surface

The hydrogenation experiments show that the presence of metallic Zn in the Ru-based catalyst has a delicate influence on

**Table 2**

Adsorption parameters corresponding to the adsorbed benzene and cyclohexene molecules with the lowest energy.

Adsorption configuration	Benzene		Cyclohexene
	hcp	fcc	atop
$\Delta H$ (kJ/mol)	-139.51	-139.92	-57.47
<sup>a</sup> C=C bond length (Å)	1.44	1.44	1.42
<sup>b</sup> $\Delta\Phi$ (eV)	-1.05	-0.99	-0.19

<sup>a</sup> Bond length of the C=C conjugate bond of a benzene molecule and a cyclohexene molecule in the vacuum is 1.40 Å and 1.34 Å, respectively.

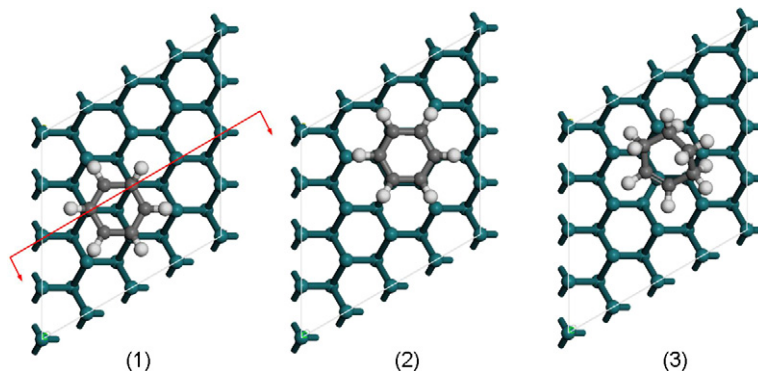
<sup>b</sup> Work function of the Ru(0001) surface: 5.17 eV.

the partial hydrogenation behavior of benzene. In the literature, it is commonly acknowledged that to prevent the re-adsorption of cyclohexene onto the catalyst surface in the middle and late reaction stage is critical to the cyclohexene yield. Along these lines, the adsorption of benzene and cyclohexene on the Ru(0001) surface and Ru-Zn/Ru(0001) surface alloy was studied, respectively.

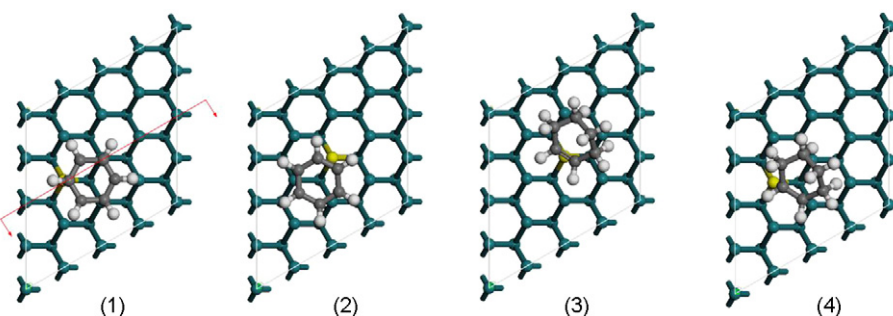
Adsorption configurations of benzene on the Ru(0001) surface can be distinguished by the position of its ring center, i.e. hcp sites or fcc sites, and by the relative position between the C atom and the surface Ru atom. Accordingly, adsorption configurations of cyclohexene can be mainly distinguished by the situation whether its C=C double bond is located at the Ru-Ru bridge site or at the atop site of the Ru atom. After configuration optimization, the most stable adsorption configurations of benzene and cyclohexene on the Ru(0001) surface are shown in Fig. 6, with their adsorption parameters listed in Table 2.

Although Fig. 6-1 and -2 illustrates the adsorbed benzene molecules with the lowest potential energy, actually the difference in heat of adsorption between them and other adsorption configurations is only within 5–10 kJ/mol, suggesting that benzene can be adsorbed on the Ru metal with multiple choices. As for cyclohexene, the heat of adsorption of configurations at the atop site is much higher than that at the bridge site by 35–40 kJ/mol. That is to say, cyclohexene is predominantly adsorbed at the atop site of the surface Ru atom. By the magnitude of the calculated heat of adsorption, it is proposed that both the adsorbed benzene and cyclohexene molecules shown in Fig. 6 are in the state of chemisorption. In addition, interaction between the Ru surface and benzene should be much stronger than that between the surface and cyclohexene.

Usually the adsorption of species with the conjugated double bond on the transition metal follows the  $\sigma$ -donation and  $\pi$ -back donation scheme. A decrease in the work function of the Ru(0001) surface ranging from -0.19 to -1.05 eV was found after the chemisorption of benzene and cyclohexene, indicating that part of the electrons are transferred from the HOMO of the adsorbates to the valence orbitals of the surface Ru atoms. Basically, variation



**Fig. 6.** Adsorbed benzene and cyclohexene molecules on the Ru(0001) surface with the lowest energy; the red line marks the cross-section for the charge density analysis; (1) benzene/hcp site, (2) benzene/fcc site, and (3) cyclohexene/atop site. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)



**Fig. 7.** Initial guess to the adsorption configuration of benzene and cyclohexene molecules on the Ru-Zn/Ru(0001) surface in the case of the adsorption site involving a Zn atom; The yellow ball represents a Zn atom; the red line marks the cross-section for the charge density analysis; benzene: (1) hcp/c<sub>1</sub> site, (2) hcp/c<sub>2</sub> site; cyclohexene: (3) atop site, (4) Ru-Zn bridge site. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

of the work function listed in Table 2 is in accordance with the calculated heat of adsorption.

It is noteworthy that cyclohexene is preferentially adsorbed at the bridge site on the closest packing plane (111) of the commonly used group VIII metals with the face-centered cubic lattice [23,24]. The unexpected adsorption behavior of cyclohexene on the Ru metal cannot be explained by the spatial matching between the distance of surface atoms and the HOMO of the cyclohexene molecule, which means it may be resulted from the unique valence structure of the Ru atoms.

#### 3.4. Adsorption of benzene and cyclohexene on the Ru-Zn/Ru(0001) surface

On introducing metallic Zn onto the Ru(0001) surface, adsorption of adsorbates on the surface alloy is much more complicated than that on the Ru(0001) surface since the adsorption site may be directly related to or in a certain distance from the Zn atom. Furthermore, surface concentration of the Zn atom will surely affect the adsorption configuration. In this paper, the simplest situation in which only a singular Zn atom is involved in the supercell is considered. At that time, surface concentration of the Zn atom is 1/16.

First consider the cases in which the adsorption sites of benzene and cyclohexene are directly related to the Zn atom. Fig. 7-1 and -2 illustrates the initial guess to the adsorbed benzene molecules whose ring center is located at the hcp site. Their C atoms or C=C double bonds might be at the atop site of the Zn atom, respectively. Fig. 7-3 and -4 illustrates the initial guess to the adsorbed cyclohexene molecules whose C=C double bond is placed at the atop site of the Zn atom or at the Ru-Zn bridge site. Then, optimization was performed on the basis of the above mentioned configurations.

For benzene adsorbed on the Zn atom involved sites, the heat of adsorption of the optimized configurations decreases dramatically by about 65% compared with that of the similar configurations on the Ru(0001) surface; refer to Table 3. Actually, benzene molecules lean on the surface alloy at an angle of 10° with a slightly distorted ring structure. One might deduce that such a sloping configuration is resulted from the repulsion from the Zn atom to the benzene ring, and it was confirmed by the subsequent charge density analysis of the adsorbed benzene molecule on the Ru(0001) surface and

**Table 3**

Adsorption parameters of the adsorbed benzene and cyclohexene molecules on the Ru-Zn/Ru(0001) surface in the case of adsorption sites involving a Zn atom.

	Benzene		Cyclohexene	
Initial position	hcp/c <sub>1</sub>	hcp/c <sub>1</sub>	atop	Bridge Zn-Ru
Final position	hcp/c <sub>1</sub>	hcp/c <sub>1</sub>	atop	Bridge Ru-Ru
ΔH (kJ/mol)	-47.51	-50.92	<10	-15.29

**Table 4**

Adsorption parameters of the adsorbed benzene and cyclohexene molecules on the Ru-Zn/Ru(0001) surface in the case of adsorption sites in varied distance from the Zn atom.

	Benzene		Cyclohexene	
Adsorption configuration	Fig. 9-1	Fig. 9-2	Fig. 9-3	Fig. 9-4
ΔH (kJ/mol)	-142.53	-142.44	-32.76	-34.95

on the Ru-Zn/Ru(0001) surface alloy. The analysis is based on the cross-section marked in Figs. 6-1 and 7-1, with the results presented in Fig. 8. On the Ru(0001) surface, a relatively dense charge density between the surface and benzene ring is observed, which means a strong bonding between them. As for the situation on the surface alloy, no charge is observed between the Zn atom and the C atom above it. At the same time, charge density between the other C atoms of the benzene ring and the surface Ru atom is also lower than the corresponding value on the Ru(0001) surface. Nevertheless, benzene still can be steadily adsorbed at the Zn atom involved sites in spite of the decreased overlap between the valence orbitals of the surface Ru atom and the HOMO of the benzene molecule.

Apparently, the repulsion from the surface Zn atom to the benzene ring may also occur in the case of cyclohexene adsorption. After configuration optimization, it is found that the heat of adsorption of the adsorbed cyclohexene molecule with the C=C double bond located at the atop site of the Zn atom is only less than 10 kJ/mol, suggesting that it is in the state of physisorption. Furthermore, for the cyclohexene molecule initially placed at the Ru-Zn bridge site as shown in Fig. 7-4, without exception the olefinic C atom originally above the Zn atom migrates to the atop site of the neighboring Ru atom and forms a Ru-Ru bridge configuration. In other words, the presence of metallic Zn in the Ru-based catalyst leads to a direct decrease in the sites for the chemisorption of cyclohexene.

The following calculations consider the situations in which no Zn atom is directly involved in the adsorption site of benzene and cyclohexene. Fig. 9-1 and -2 illustrates the adsorbed benzene molecules in varied distance from the Zn atom, while Fig. 9-3 and -4 shows the similar cases of the adsorbed cyclohexene molecules. According to the calculated heat of adsorption listed in Table 4, adsorption of benzene on the alloy catalyst recovers rapidly once its adsorption site leaves away from the Zn atom. On the contrary, the adsorption of cyclohexene fails to recover although its adsorption site is already in a certain distance from the Zn atom, which means the whole alloy catalyst considered in this study is partly passivated for cyclohexene adsorption. Such a passivation is also clearly embodied in the red shift of C=C stretching frequency of the adsorbed cyclohexene molecule on the Ru(0001) surface and Ru-Zn/Ru(0001) surface alloy; refer to Table 5. On the whole, red shift of the C=C stretching frequency of an adsorbed cyclohexene

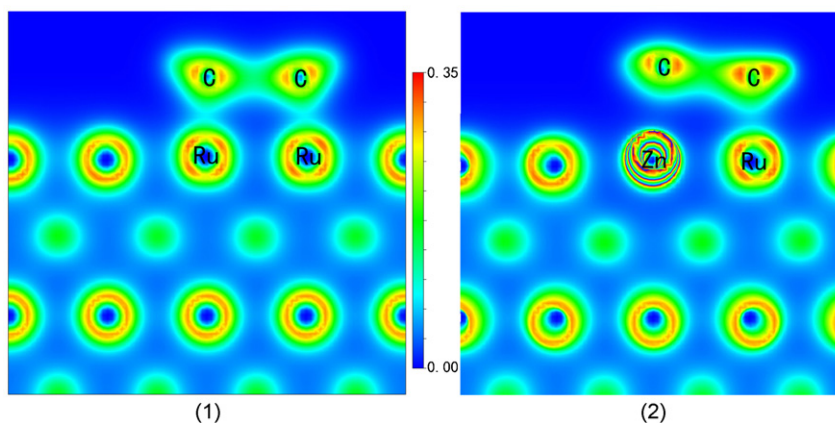


Fig. 8. Charge density on the cross-section of the benzene molecule adsorbed Ru(0001) surface and Ru-Zn/Ru(0001) surface; (1) based on Fig. 6-1, (2) based on Fig. 7-1.

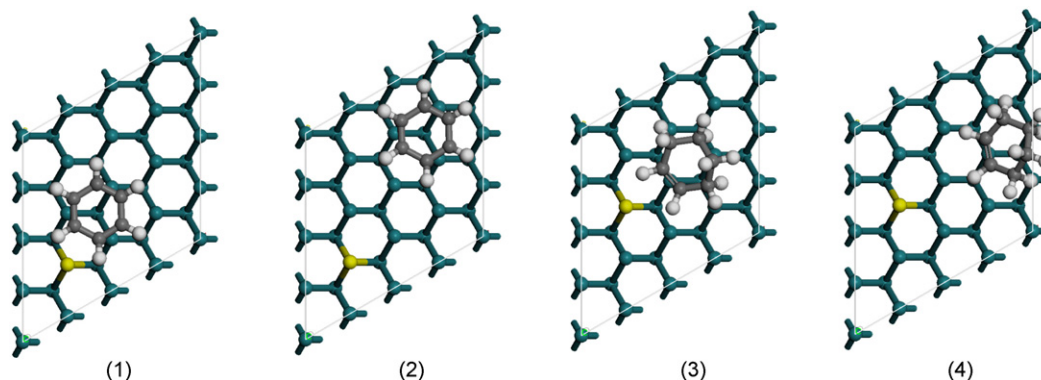


Fig. 9. Adsorbed benzene and cyclohexene molecules on the Ru-Zn/Ru(0001) surface whose adsorption site leaves away from the Zn atom; the yellow ball represents a Zn atom; benzene: (1) and (2) hcp/c<sub>2</sub> site; cyclohexene: (3) and (4) atop site. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

molecule is in accordance with the interaction strength between the surface and the cyclohexene molecule. A decreased red shift on the alloy catalyst indicates that chemisorption of cyclohexene on the whole alloy catalyst is depressed.

The above discussion shows that chemisorption of benzene and cyclohexene on the metallic Zn modified Ru-based catalyst should be both restrained. However, essential differences can be found as follows.

- Benzene still can be chemisorbed at the site involving a Zn atom; besides, the presence of metallic Zn virtually has no influence on the adsorption of benzene at the neighboring site.
- Apart from a direct reduction in chemisorption sites, the whole modified catalyst is partly passivated for the adsorption of cyclohexene.

It can be reasonably proposed that, with the further elevation of surface concentration of metallic Zn, not only the chemisorption of cyclohexene but also that of benzene will be eventually prohibited on the modified catalyst.

Table 5

Red shift of C=C stretching frequency of a cyclohexene molecule adsorbed on the Ru(0001) surface and Ru-Zn/Ru(0001) surface alloy.

	Ru(0001)	Ru-Zn/Ru(0001)	
Adsorption configuration	Fig. 6-3	Fig. 9-3	Fig. 9-4
<sup>a</sup> $\Delta\nu$ (cm <sup>-1</sup> )	-171.81	-149.4	-152.2

<sup>a</sup>  $\nu_{\text{C=C stretching}}$  of a cyclohexene molecule in the vacuum: 1614.39 cm<sup>-1</sup>.

It should be noticed that partial hydrogenation of benzene occurs on the surface of Ru-based catalyst suspended in the water phase. The above calculations are all based on the adsorption in the vacuum; therefore, it is necessary to verify whether the same conclusion can be drawn in the presence of co-adsorption of water molecules. Subsequent calculation shows that on the Ru(0001) surface water molecules are adsorbed at the atop site of the surface Ru atom with the oxygen atom pointing to the surface. The corresponding heat of adsorption is only slightly lower than that of cyclohexene, suggesting that the Ru metal is highly hydrophilic. Re-adsorption of cyclohexene thus can be effectively restrained due to the hydrophilic nature of the Ru-based catalyst. As for the Ru-Zn alloy, the calculated heat of adsorption of water molecules at the atop site of Zn atoms is less than 10 kJ/mol, indicating that no chemisorption can be formed on the Zn atom. That is to say, to introduce metallic Zn into the Ru-based catalyst results in a local depression to the hydrophilicity of the catalyst surface. Fortunately, such a depression has no promotion to the chemisorption of cyclohexene since it cannot be chemisorbed on the Zn atom related sites either. It is therefore confirmed that, whether there is competitive adsorption of water molecules or not, the conclusion about the adsorption behavior of benzene and cyclohexene on the metallic Zn modified Ru-based catalyst is just the same.

### 3.5. Effect of metallic Zn on the hydrogenation behavior

Consider first the partial hydrogenation of benzene over the traditional Ru-based catalyst. In the initial stage of reaction, only benzene exists in the organic phase and it is adsorbed on the

catalyst surface with absolute priority. However, elevation of cyclohexene concentration in the organic phase will lead to an inevitable increase in its surface concentration on the catalyst surface regardless of the fact that the heat of adsorption of benzene is much higher than that of cyclohexene. In the middle stage of reaction, one may observe that the yield of by-product cyclohexane increases continuously and the yield of cyclohexene nearly keeps unchanged. At that moment, restriction to the undesired side reaction from cyclohexene to cyclohexane depends mainly on the presence of the water phase and on the adsorption of  $Zn^{2+}$  at the most active hydrogenation sites.

When the partial hydrogenation of benzene is conducted over the metallic Zn modified Ru-based catalyst, the situation is quite different. In the initial reaction stage, benzene is also preferentially adsorbed on the catalyst surface and is hydrogenated to cyclohexene. Because of the depression to the benzene adsorption on the alloy catalyst, a decreased conversion rate of benzene should be experimentally observed. In the middle stage of reaction, the adsorption of benzene and cyclohexene on the catalyst surface is both restrained, but the latter is much more serious than the former. As a result, re-adsorption of cyclohexene from the organic phase to the catalyst surface is prevented not only by the water phase but also by the presence of metallic Zn on the catalyst surface. The side reaction from cyclohexene to cyclohexane therefore is effectively retarded, and now there is good chance to obtain a satisfied cyclohexene yield.

Essentially, the improvement of cyclohexene yield over the metallic Zn modified Ru-based catalyst is realized by sacrificing part of the catalytic activity. With the elevation of Zn content in the catalyst, both the side reaction from cyclohexene to cyclohexane and the partial hydrogenation from benzene to cyclohexene will be suppressed gradually. In addition, the residence time to achieve the highest cyclohexene yield will be excessively prolonged, which makes the whole process uneconomic. An optimal Zn content in the modified catalyst therefore should be experimentally determined.

#### 4. Conclusions

By introducing metallic Zn into the Ru-based catalyst in the partial hydrogenation of benzene, an improved cyclohexene yield of 44% is obtained. Surface characterizations confirm the presence of metallic Zn in the prepared Ru-Zn/ZrO<sub>2</sub> catalyst. Theoretical calculations propose that chemisorption of benzene and cyclohexene

on the Ru-Zn alloy catalyst is both restrained, the latter being much more serious than the former. The above proposal is valid no matter in the presence of or in the absence of the competitive adsorption of water molecules. In the middle and late stage of hydrogenation, re-adsorption of cyclohexene on the modified catalyst is depressed simultaneously by the presence of metallic Zn on the catalyst surface and by the presence of the water phase, which is unfavorable for the undesired side reaction from cyclohexene to cyclohexane. A reduced catalytic activity but improved selectivity to cyclohexene therefore is experimentally observed. Due to the different influence of metallic Zn on the benzene conversion rate and on the selectivity to cyclohexene, a satisfied cyclohexene yield can only be obtained over the modified catalyst with the optimal Zn content.

#### References

- [1] W.C. Drinkard Jr., NL Patent 7,205,832 (1972) to E.I. DU PONT DE NEMOURS and COMPANY.
- [2] O. Mitsui, Y. Fukuoka, US Patent 4,678,861 (1987) to Asahi Chemical Company.
- [3] H. Nagahara, M. Konishi, US Patent 4,734,536 (1988) to Asahi Kasei Kogyo Kabushiki Kaisha.
- [4] H. Nagahara, M. Ono, M. Konishi, Y. Fukuoka, Appl. Surf. Sci. 121 (1997) 448–451.
- [5] P. Kluson, L. Cerveny, Appl. Catal. A 128 (1995) 13–31.
- [6] Anderson Jr., C. Kemball, Aust. J. Chem. 10 (1957) 409–415.
- [7] C. Hoang-Van, G. Tournier, S.J. Teichner, J. Catal. 86 (1984) 210–214.
- [8] P. Staiti, S. Galvagno, P. Antonucci, A. Rositani, P. Vitarelli, React. Kinet. Catal. Lett. 26 (1984) 111–116.
- [9] D.P. Harrison, H.F. Rase, Ind. Eng. Chem. Fundam. 6 (1967) 161–169.
- [10] L. Ronchin, L. Toniolo, Catal. Today 66 (2001) 363–369.
- [11] Sung-Cheng Hu, Yu-Wen Chen, Ind. Eng. Chem. Res. 40 (2001) 6099–6104.
- [12] E.V. Spinacé, J.M. Vaz, Catal. Commun. 4 (2003) 91–96.
- [13] G.Y. Fan, R.X. Li, X.J. Li, H. Chen, Catal. Commun. 9 (2008) 1394–1397.
- [14] S.C. Liu, Z.Y. Liu, S.H. Zhao, Y.M. Wu, Z. Wang, P. Yuan, J. Nat. Gas Chem. 15 (2006) 319–326.
- [15] S.C. Liu, Z.Y. Liu, Z. Wang, Y.M. Wu, P. Yuan, Chem. Eng. J. 139 (2008) 157–164.
- [16] J.Q. Wang, Y.Z. Wang, S.H. Xie, M.H. Qiao, H.X. Li, K.N. Fan, Appl. Catal. A 272 (2004) 29–36.
- [17] J. Bu, J.L. Liu, X.Y. Chen, J.H. Zhuang, S.R. Yan, M.H. Qiao, H.Y. He, K.N. Fan, Catal. Commun. 9 (2008) 2612–2615.
- [18] J.L. Liu, L.J. Zhu, Y. Pei, J.H. Zhuang, H. Li, H.X. Li, M.H. Qiao, K.N. Fan, Appl. Catal. A 353 (2009) 282–287.
- [19] P.Q. Yuan, B.Q. Wang, Y.M. Ma, H.M. He, Z.M. Cheng, W.K. Yuan, J. Mol. Catal. A: Chem. 301 (2009) 140–145.
- [20] V.I. Nefedov, J. Electron. Spectrosc. Relat. Phenom. 25 (1982) 29–47.
- [21] S.W. Gaarenstroom, N. Winograd, J. Chem. Phys. 67 (1977) 3500–3506.
- [22] L. Ley, S.P. Kowalczyk, F.R. McFeely, R.A. Pollak, D.A. Shirley, Phys. Rev. B 8 (1973) 2392–2402.
- [23] M. Saeys, M.F. Reyniers, M. Neurock, G.B. Marin, Surf. Sci. 600 (2006) 3121–3134.
- [24] F. Delbecq, F.V. Maeder, C. Becker, J. Breitbach, K. Wandelt, J. Phys. Chem. C 112 (2008) 555–566.