



## Hydrogenation of cyclohexene over Ru–Zn/Ru(0001) surface alloy: A first principles density functional study

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### ABSTRACT

In this work, the hydrogenation of cyclohexene over Ru–Zn/Ru(0001) surface alloy was investigated by a DFT study so as to improve the understanding of the catalytic mechanism of the partial hydrogenation of benzene to cyclohexene over Ru–Zn alloy catalyst. Calculation results show that the presence of Zn atoms on the surface alloy results in not only a direct decrease in sites for the chemisorption of cyclohexene but also a depressed adsorption capability of the neighboring surface Ru sites. For an adsorbed cyclohexene molecule, whether the subsequent hydrogenation can be readily performed actually is determined by the relative position among the Zn atom, the H atom, and the adsorbed cyclohexene molecule. In most cases, the hydrogenation is forbidden because of the repulsion from Zn atoms to the nearby H atoms. Only in the specific situations in which the H atom participating in the reaction is not immediately close to the Zn atom, can the hydrogenation be accomplished with a relatively lower activation energy compared with the reactions on the Ru(0001) surface. From the perspectives of adsorption and reaction kinetics, Ru-based catalyst modified by metallic Zn is no longer suitable for the hydrogenation of cyclohexene, which is supposed to be crucial to the improvement of cyclohexene yield in the partial hydrogenation of benzene over Ru–Zn alloy catalyst.

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### 1. Introduction

Partial hydrogenation of benzene to cyclohexene, which was first industrialized in a tetra-phase hydrogenation system by Asahi Chemical Industry Co. in 1989, is of commercial interest in nylon industry. Different from the traditional hydrogenation processes, a water phase containing a large amount of dissolved zinc sulfate is introduced into the partial hydrogenation of benzene, with the hydrophilic Ru-based catalyst suspended in the water phase [1,2]. Since the solubility of cyclohexene in the water phase is much lower than that of benzene, the presence of water phase can effectively prevent the re-adsorption of cyclohexene from the organic phase onto the catalyst surface. Zinc ions in the water phase are suggested to serve a dual purpose. On the one hand, Zn<sup>2+</sup> ions presented on the catalyst surface improve the hydrophilicity of Ru-based catalyst. On the other hand, deep hydrogenation of benzene is suppressed due to the adsorption of Zn<sup>2+</sup> at the highly active catalytic sites.

Despite numerous patents and papers on benzene partial hydrogenation, efficient catalysts are mainly confined to ruthenium black or its alloys [3–8]. Recently a novel Ru–Zn alloy catalyst was applied in the partial hydrogenation of benzene to cyclohexene [9]. In

authors' laboratory, a satisfied cyclohexene yield up to 44% was obtained over the Ru–Zn alloy. For the most Ru-based catalytic systems, zinc element is mainly in the form of Zn<sup>2+</sup> dissolved in the water phase or adsorbed on the catalyst surface. However, for the Ru–Zn alloy catalyst, part of zinc element is in the form of atomic state on the catalyst surface or in the bulk phase of the catalyst. Experiments over the Ru–Zn alloy catalyst indicated that, at a fixed Zn<sup>2+</sup> concentration in the water phase, an increase in the zinc atom content in the Ru–Zn alloy catalyst may lead to an improved selectivity to cyclohexene but a monotonously decreased catalytic activity. Theoretical calculation suggested that the adsorbed Zn<sup>2+</sup> ions can be reduced by the adsorbed H atoms [10]. That is to say, the existence of Zn atoms in the Ru-based catalytic systems is just a universal phenomenon no matter it is resulted from the reduction of the adsorbed Zn<sup>2+</sup> during the benzene hydrogenation or from that during the catalyst preparation [11–13].

Hitherto, the roles of Zn atoms in the catalytic performance of the Ru–Zn alloy catalyst and other Ru-based catalysts have not been touched in the literature. On considering this problem, related research at least can be divided into two aspects: effect of Zn atoms' existence on the adsorption of benzene and on the hydrogenation of benzene to cyclohexene; effect of Zn atoms' existence on the adsorption of cyclohexene and on the hydrogenation of cyclohexene to cyclohexane. The latter was first studied in this work by the reason that to avoid the further hydrogenation of cyclohexene on

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the catalyst surface is commonly acknowledged to be essential to the cyclohexene yield.

Although the XPS spectra have already confirmed the presence of metallic Zn in the Ru–Zn alloy catalyst, diffraction patterns of Zn element cannot be detected by XRD, suggesting that Zn atoms are highly dispersed in the alloy catalyst [9]. At present, it is difficult to determine the exact phase pattern and the corresponding lattice parameters of Ru–Zn alloy. By replacing Ru atoms with Zn atoms on the upmost layer of the Ru(0001) surface, a Ru–Zn/Ru(0001) surface alloy was used in this work to simulate the adsorption and the subsequent hydrogenation of cyclohexene on the Ru–Zn alloy catalyst.

This paper is arranged as follows. The theoretical background of calculation is first introduced. Then, the adsorption behavior of cyclohexene on the Ru(0001) surface and on the Ru–Zn/Ru(0001) surface alloy was compared based on the conformation optimization, vibration frequency analysis, and work function analysis. After that, potential energy profiles of the cyclohexene hydrogenation on the Ru(0001) surface as well as on the Ru–Zn surface alloy were located, followed by a discussion on the effect of Zn atoms on the reaction kinetics of cyclohexene hydrogenation. Finally, the unique performance of the Ru–Zn alloy catalyst applied in the partial hydrogenation of benzene to cyclohexene is further explicated on the basis of the above discussion.

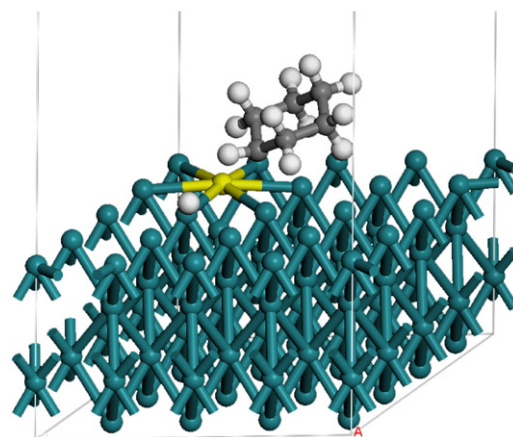
## 2. Theoretical method

A cyclohexene molecule can be in the half-chair conformation or in the boat conformation in the gas phase, the former having a lower enthalpy than the latter by 22.90 kJ/mol. Although the adsorbed boat cyclohexene in the di- $\sigma$  mode was proposed to be the most stable conformation on the Pt(111) surface, there is no related report on the adsorption state of cyclohexene on the Ru crystal surface [14]. Cyclohexene molecules in the half-chair conformation therefore were considered as the adsorbates and were applied in the subsequent hydrogenation.

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 method (PAW) and the generalized gradient approximation (GGA) level with the functional of PW91 were used. A cutoff of 400 eV has been applied to the plane wave basis set, which allows 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.

In most calculations, the Ru–Zn/Ru(0001) surfaces were modeled by a periodic 4 × 4 four-layer slab in which only the first layer contains a single Zn atom; refer to Fig. 1. Only in the calculations on the work function of the Ru–Zn/Ru(0001) surface at varied Zn surface concentration, the first layer may contain more than one Zn atom. For the remaining part of the slab, the same metal interatomic distance was used in the case of pure ruthenium and in the case of the alloys. 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 chosen corresponding to the size of the supercell. 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.



**Fig. 1.** Periodic supercell approach for cyclohexene adsorption or hydrogenation on the Ru–Zn/Ru(0001) surface alloy; the yellow ball means a Zn atom and the blue ones Ru atoms.

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

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

where  $E_{\text{Slab}}$  and  $E_{\text{Molecule}}$  are the total energies of the relaxed bare slab and of the free cyclohexene molecule, respectively, while  $E_{\text{Adsorption}}$  represents the total energy of the relaxed surface/cyclohexene adsorption system.

The variation of work function ( $\Delta\Phi$ ) of the catalyst surface due to the cyclohexene 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/cyclohexene adsorption system and of the relaxed bare slab, respectively.

A climbing image nudged elastic band (NEB) method was applied to locate the minimum energy path (MEP) and the transition states for the cyclohexene hydrogenation on the catalyst surface. Six interpolated images between the initial and final positions were connected by springs and relaxed simultaneously to the MEP.

## 3. Results and discussion

### 3.1. Adsorption of cyclohexene on the Ru(0001) surface

When a cyclohexene molecule is adsorbed on the Ru(0001) surface, it can be in the di- $\sigma$  (bridge) or  $\pi$  (on top) mode in which two olefinic carbon atoms interact with two or one surface Ru atoms, respectively. Detailed adsorption modes can be further distinguished by the location of the ring center of cyclohexene molecules on the surface, i.e. three-fold fcc sites or three-fold hcp sites. The calculated heat of adsorption and conformation parameters with respect to the different adsorption modes are listed in Table 1.

**Table 1**  
Adsorption parameters with respect to different adsorption modes of cyclohexene on the Ru(0001) surface.

Adsorption modes	di- $\sigma$ /fcc	di- $\sigma$ /hcp	$\pi$ /fcc	$\pi$ /hcp
$\Delta H$ (kJ/mol)	–15.29	–24.06	–50.90	–57.47
C=C bond length (Å)	1.448	1.462	1.413	1.417
C–Ru distance (Å)	2.261	2.252	2.303	2.285
$\Delta\Phi$ (eV)	–0.1307	–0.1404	–0.1648	–0.1895

\* C=C bond length of a half-chair cyclohexene molecule in the vacuum: 1.338 Å.

**Table 2**  
Red shift of C=C stretching vibration of a  $\pi$  bound cyclohexene molecule on the Ru(0001) surface.

	$\pi$ /fcc	$\pi$ /hcp
$\Delta\nu_{\text{C=C}}$ stretching ( $\text{cm}^{-1}$ )	-163.73	-171.81

\* $\nu_{\text{C=C}}$  stretching of a half-chair cyclohexene molecule in the vacuum = 1614.39  $\text{cm}^{-1}$ .

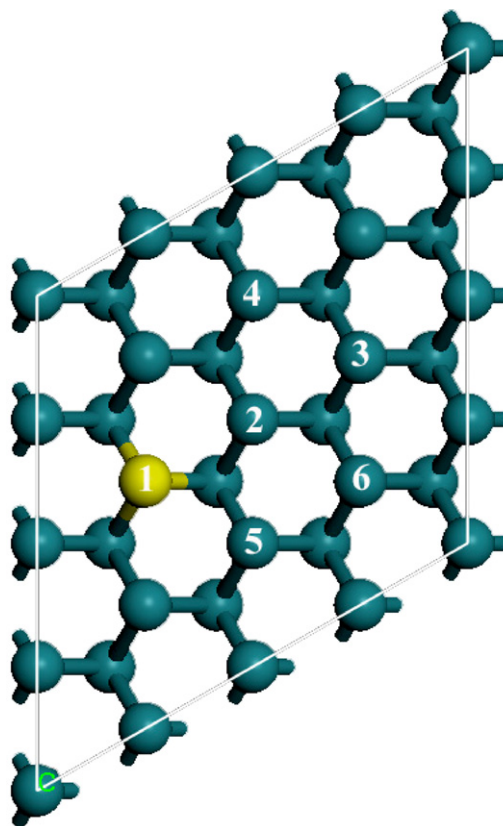
Calculation results presented in Table 1 indicate the chemisorption of cyclohexene molecules on the Ru(0001) surface. Although the average C=C bond stretching of the di- $\sigma$  bound cyclohexene molecules is longer than that of the  $\pi$  bound ones by 0.07–0.08 Å, the heat of adsorption of the former is much lower than that of the latter by about 25 kJ/mol. That is to say, cyclohexene is adsorbed on the Ru(0001) surface preferentially in the  $\pi$  mode, which is different from the situation on other commonly used metal surfaces or surface alloys [14,15]. Transition metals for hydrogenation, e.g. Ni, Pd, and Pt, have face-centered cubic crystal structure. By applying the same calculations, it is confirmed that the di- $\sigma$  bound cyclohexene molecules on the (111) surface, i.e. the closest packing plane of the above mentioned metals are stabler than those  $\pi$  bound ones. Since Ru crystal has a hexagonal crystal structure, one might consider the spatial matching between the surface atoms and the olefinic carbon atoms of cyclohexene molecules to explain the above unexpected phenomena. However, the distance between the adjacent surface atoms on the (111) surface of Ni, Pd, and Pt ranges from 2.49 to 2.78 Å, while the corresponding value on the Ru(0001) surface is 2.71 Å. It is deduced that the unique adsorption behavior of cyclohexene on the Ru(0001) surface could be resulted from the valence shell structure of Ru atoms.

Usually the adsorption of olefinic hydrocarbons on the surface of transition metal follows the  $\sigma$ -donation and  $\pi$ -back donation scheme. After the adsorption of cyclohexene molecules, work function of the Ru(0001) surface is found to decrease in varying degrees, suggesting the electron transfer from the adsorbate to the substrate. Besides, evident red shift of C=C stretching vibration for the adsorbed cyclohexene molecule is also observed, which means a weakened C=C bond strength after adsorption. The magnitude of  $\Delta\Phi$  and red shift is approximately in accordance with the interaction intensity between the adsorbed cyclohexene molecules and the surface; refer to Tables 1 and 2. On adsorption, cyclohexene molecules are now activated for the following hydrogenation.

### 3.2. Adsorption of cyclohexene on the Ru–Zn/Ru(0001) surface alloy

On forming the Ru–Zn surface alloy, there are multiple possibilities for the chemisorption of cyclohexene with respect to the different surface concentration and the location of Zn atoms. Consider a simple situation shown in Fig. 2 in which the surface concentration of the Zn atom is 1/16. Atoms with the numerical notation represent the possible sites for cyclohexene adsorption, the yellow one with the label No.1 being a Zn atom. Cyclohexene molecules can be adsorbed in the optional modes as follows:  $\pi$  mode above the Zn atom (designated as site 1) or above the surface Ru atom (sites 2, 3, etc.); di- $\sigma$  mode crossing Ru–Zn sites (sites 1–2, 1–5, etc.) or crossing Ru–Ru sites (sites 2–5, 3–6, etc.). The conformation optimization then was applied based on the possible adsorption sites mentioned above.

For the cyclohexene molecule initially placed in the  $\pi$  mode above the Zn atom (site 1), after optimization its C=C bond length is nearly equal to the corresponding value in the vacuum and the calculated heat of adsorption is less than 10 kJ/mol. That is to say, the  $\pi$  bound cyclohexene molecule above the Zn atom is in the state of physisorption.



**Fig. 2.** Ru–Zn/Ru(0001) surface alloy; the yellow ball represents a Zn atom and blue ones Ru atoms; atoms with numerical notation are the possible sites for cyclohexene adsorption.

As for the cyclohexene molecules initially placed in the di- $\sigma$  mode crossing Ru–Zn sites (sites 1–2, 1–5, etc.), without exception, the olefinic carbon atom on the Zn atom eventually migrates onto the neighboring Ru atoms after optimization. Actually, their final conformations are similar to those in the di- $\sigma$  mode crossing Ru–Ru sites (sites 2–5, 3–6, etc.). At that time, the corresponding heat of adsorption is slightly lower than that of those di- $\sigma$  bound molecules on the Ru(0001) surface.

Further conformation optimizations on the  $\pi$  bound cyclohexene molecule on the surface Ru atom (sites 2 and 3) were applied, with the results presented in Table 3. Compared with the same situation on the Ru(0001) surface, one can notice a sharp decrease in the heat of adsorption by about 20 kJ/mol. At the same time, other adsorption parameters, such as the  $\Delta\nu_{\text{C=C}}$  and  $\Delta\Phi$ , are all lower than the relevant values on the Ru(0001) surface. In other words, chemisorption of cyclohexene on the Ru atoms neighboring the Zn atom is seriously depressed, and it fails to recover when the adsorption site moves away from the Zn atom.

By the consideration that work function of a substrate surface can be used to characterize its surface properties, work function of the Ru–Zn surface alloy at varied surface concentration of Zn atoms was calculated, with the results presented in Table 4. It was found that work function of the Ru–Zn surface alloy decreases monotonously along with the elevation in the Zn atom concentration. Considering the depressed chemisorption of cyclohexene on the Ru–Zn surface alloy, it can be proposed that the adsorption behavior of cyclohexene on the Ru–Zn surface alloy might also be a sensitive function of the surface concentration of Zn atoms.

Since the Ru-based catalyst is suspended in the water phase, co-adsorption of water molecules might have influence on the adsorption behavior of cyclohexene. Calculation results show

**Table 3**  
Adsorption parameters of a  $\pi$  bound cyclohexene molecule on the Ru–Zn/Ru(0001) surface.

No.	Adsorption mode and site	$\Delta H$ (kJ/mol)	C=C length (Å)	C–Ru distance (Å)	$\Delta\nu_{C=C}$ (cm <sup>-1</sup> )	$\Delta\phi$ (eV)
1	$\pi$ /hcp/site 2	-32.76	1.408	2.483	-149.6	-0.1401
2	$\pi$ /hcp/site 3	-34.95	1.412	2.445	-152.2	-0.1418

**Table 4**  
Work function of the Ru–Zn/Ru(0001) surface at different Zn atom surface concentration.

Surface concentration of Zn atoms	Work function (eV)
0	5.161
1/16	5.135
1/8	5.122

that on the Ru(0001) surface water molecules are preferentially adsorbed at the atop sites of the surface Ru atoms with the oxygen atom pointing to the surface. The calculated heat of adsorption of water on the Ru(0001) surface is only slightly lower than that of cyclohexene, suggesting that the Ru catalyst is highly hydrophilic. Adsorption of cyclohexene on the Ru catalyst therefore is suppressed due to the competitive adsorption of water molecules. As concerns the Ru–Zn/Ru(0001) surface, the calculated heat of adsorption of water molecules at the atop sites of the Zn atom is less than 10 kJ/mol. That is to say, the presence of Zn atoms results in local depression to the hydrophilicity of the catalyst surface. It is noteworthy that such a depression actually has no promotion to the adsorption of cyclohexene molecules because they cannot be chemisorbed on the Zn atoms either. No matter in the absence of or in the presence of water molecules, the Zn atoms modified Ru crystal surface leads to not only a direct decrease in the sites for the chemisorption of cyclohexene but also a passivation to the neighboring Ru atoms. Such a passivation almost covers the whole Ru–Zn surface alloy applied in this work. Ru–Zn surface alloy thus is considered to be much more unsuitable for the chemisorption of cyclohexene.

### 3.3. Reaction kinetics of cyclohexene hydrogenation over Ru–Zn surface alloy

Cyclohexene molecules are adsorbed preferentially in the  $\pi$  mode on the Ru(0001) surface and Ru–Zn/Ru(0001) surface, so only  $\pi$  bound cyclohexene molecules are adopted in the further studies on the reaction kinetics of cyclohexene hydrogenation.

MEPs of the cyclohexene hydrogenation on the Ru(0001) surface were first located, with the corresponding transition states

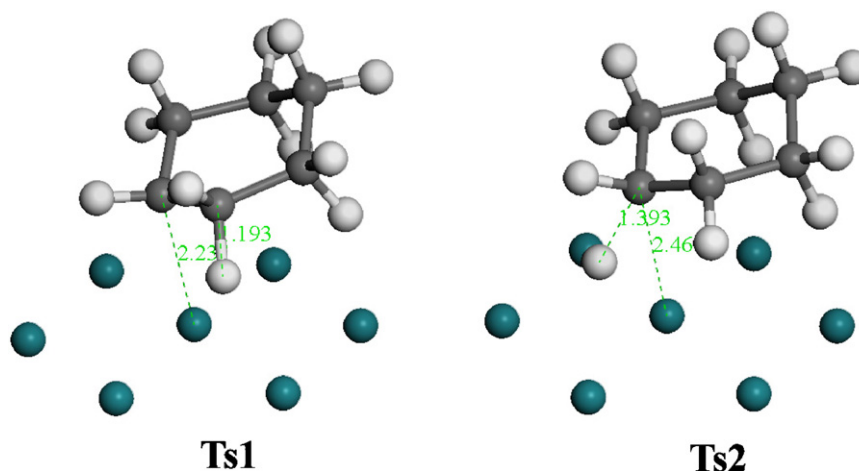
**Table 5**  
Activation energy of cyclohexene hydrogenation in both positive and negative directions.

	Ru(0001) surface		Ru–Zn/Ru(0001) surface	
	Ea <sup>+</sup> (kJ/mol)	Ea <sup>-</sup> (kJ/mol)	Ea <sup>+</sup> (kJ/mol)	Ea <sup>-</sup> (kJ/mol)
Ts1	79.93	44.33	69.27	35.61
Ts2	62.62	88.41	64.13	94.76

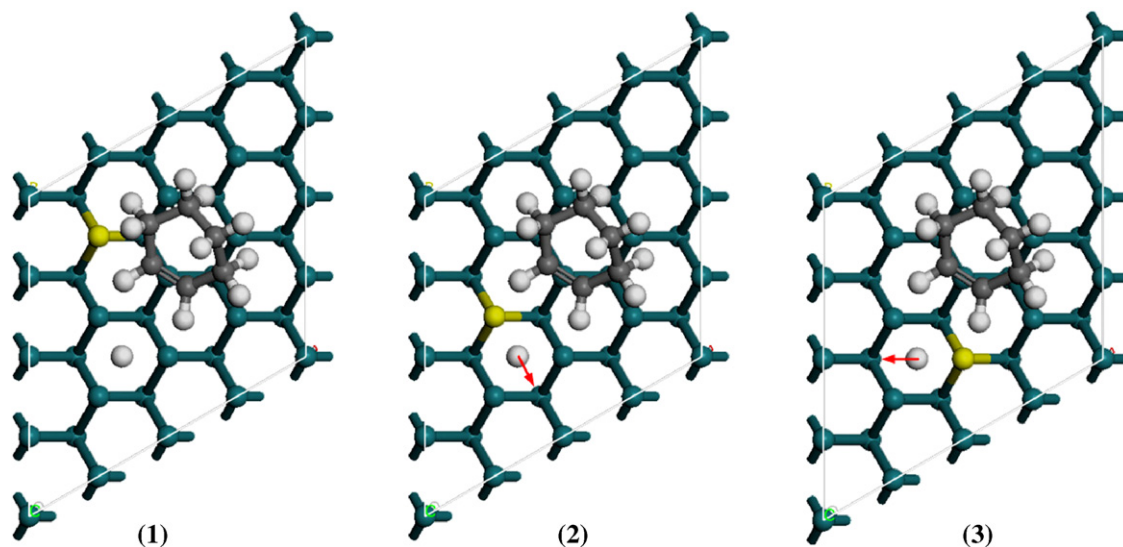
found; refer to Fig. 3. For clarity, Figs. 3 and 5 focus only on the adsorption site of the transition states and do not show the full supercell. During the first hydrogenation step, the H atom initially located in an fcc site moves towards the  $\pi$  bound cyclohexene molecule by surface diffusion, bonding with the surface Ru atom immediately adjacent to the adsorption site of cyclohexene. After a further migration towards one of the olefinic carbon atoms of the cyclohexene molecule, the intermediate product hydrocyclohexene is formed through a transition state Ts1. Instead of the original half-chair conformation, the hydrocyclohexene now is in the chair conformation. As concerns the second hydrogenation step, the H atom first bonds simultaneously with two surface Ru atoms adjacent to the adsorbed hydrocyclohexene. After a further approach, the final product cyclohexane in the chair conformation is obtained through a transition state Ts2; refer to Fig. 3. Cyclohexane molecules are physically adsorbed on the Ru(0001) surface.

Based on the energy difference of the MEPs, one can calculate the activation energy of cyclohexene hydrogenation on the Ru(0001) surface in both positive and negative directions. As the calculated data in Table 5 show, activation energy of the first hydrogenation step is higher than that of the second step by 17.31 kJ/mol, indicating that the former is the rate-determining step of the cyclohexene hydrogenation on the Ru(0001) surface.

In terms of the cyclohexene hydrogenation on the Ru–Zn/Ru(0001) surface, a number of factors might have influence on the location of the MEP as well as the conformation of the transition states: the surface concentration of Zn atoms, relative position among the Zn atom and the involved reactants, etc. Consider the first step of cyclohexene hydrogenation on the Ru–Zn surface alloy shown in Fig. 4. A cyclohexene molecule is



**Fig. 3.** Transition states of cyclohexene hydrogenation on the Ru(0001) surface.



**Fig. 4.** Initial guess of the reactant of cyclohexene hydrogenation; yellow balls represent the possible location of the Zn atom; red arrows are the moving direction of the H atom during the conformation optimization.

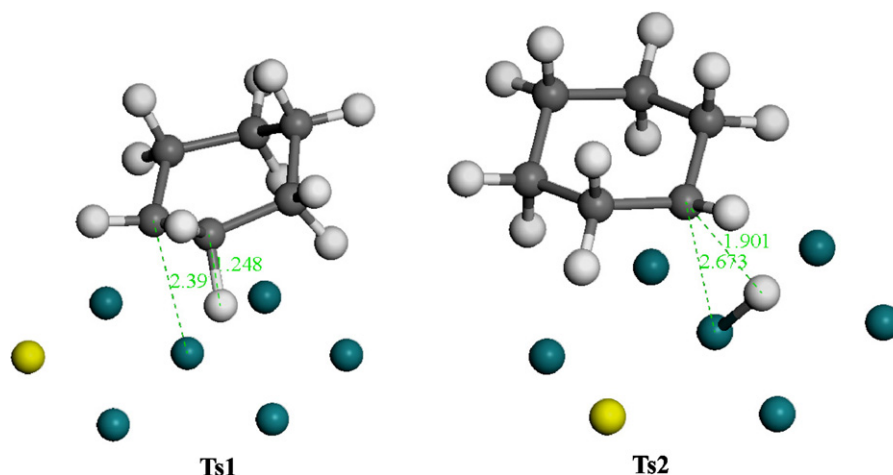
adsorbed in the  $\pi$  mode at the center of the supercell, and the H atom participating in the hydrogenation is initially placed at a neighboring fcc site which is favorable for the subsequent reaction. As for the Zn atom, it may be located immediately close to or in a certain distance with the H atom. Conformations presented in Fig. 4.1–4.3 are considered as the initial guess for the reactant involved in the first step of cyclohexene hydrogenation on the Ru–Zn surface alloy.

In the case of the Zn atom immediately close to the H atom shown in Fig. 4.2–4.3, optimization results show that the H atom initially placed at the fcc site will migrate to the neighboring hcp site because of the repulsion from the Zn atom. Furthermore, MEP of the first hydrogenation step cannot be located when these optimization results are considered as the reactants for the subsequent hydrogenation reaction. In other words, if a Zn atom is located at some specific positions near the adsorbed cyclohexene, the hydrogenation virtually is forbidden. Only in the case of the Zn atom in a certain distance with the H atom shown in Fig. 4.1, can the H atom maintain its initial position. At that time, MEP of the first hydrogenation step can be readily located when the optimization result is considered as the reactant for the hydrogenation reaction.

The situation mentioned above is also observed in the second step of cyclohexene hydrogenation on the Ru–Zn surface alloy.

Hereby, the following discussion on the reaction kinetics of cyclohexene hydrogenation on the Ru–Zn surface alloy only deals with the cases in which the Zn atom is not immediately adjacent to the H atom. Detailed NEB calculations suggest that the MEP profiles and the conformation of transition states of cyclohexene hydrogenation on the Ru–Zn surface alloy are similar to those on the Ru(0001) surface; refer to Fig. 5. Compared with the reaction occurred on the Ru(0001) surface, one may find that the activation energy of the first hydrogenation step on the Ru–Zn surface alloy decreases by 10.66 kJ/mol and that of the second step increases by 1.51 kJ/mol; refer to Table 5. Accordingly, both of the two fundamental hydrogenation steps almost have the same influence on the reaction kinetics.

The above calculations on the hydrogenation kinetics suggest that cyclohexene hydrogenation on the Ru–Zn/Ru(0001) surface depends heavily on the relative position among the Zn atom, the H atom, and the adsorbed cyclohexene or hydrocyclohexene. In most cases, the hydrogenation is prohibited due to the repulsion from the Zn atom to the adjacent H atom. Only in a specific situation in which the H atom is in a certain distance with the Zn atom, can the hydrogenation be successfully accomplished. From the statistical point of view, it is concluded that the reaction kinetics of cyclohexene hydrogenation are seriously restricted on the Ru–Zn surface alloy.



**Fig. 5.** Transition states of cyclohexene hydrogenation on the Zn–Ru/Ru(0001) surface alloy; yellow balls represent Zn atoms.

### 3.4. Effect of Zn atoms' modification on the partial hydrogenation of benzene

Consider the partial hydrogenation of benzene on the Ru(0001) surface. Since the activation energy of the rate-determining step of cyclohexene hydrogenation is in the same magnitude with that of benzene hydrogenation (77.49 kJ/mol), cyclohexene yield is mainly controlled by the adsorption behavior of the involved species. Initially benzene is adsorbed on the catalyst surface with the overwhelming priority due to the following reasons: the concentration of benzene in the feed is relatively high; the solubility of benzene in the water phase is 17 times higher than that of cyclohexene at 418 K; and the heat of adsorption of benzene on the catalyst surface is twice that of cyclohexene. A large amount of cyclohexene therefore is obtained in the initial stage of hydrogenation. Although water phase may partly prevent the re-adsorption of cyclohexene from the organic phase to the catalyst surface, gradually the surface concentration of cyclohexene on the catalyst surface becomes comparable with that of benzene along with the increase in the cyclohexene concentration in the organic phase. One can observe that the yield of cyclohexene keeps unchanged in the middle stage of hydrogenation, while the yield of undesired product cyclohexane increases sharply.

When metallic Zn is introduced into the Ru-based catalyst, the hydrogenation of both benzene and cyclohexene should be suppressed. According to the recently completed calculations on the benzene adsorption on the Ru–Zn surface alloy, the presence of Zn atoms has a relatively minor influence on the benzene adsorption over that of cyclohexene adsorption. In view of the experimentally testified higher cyclohexene yield over the Ru–Zn alloy catalyst, it is proposed that in the initial reaction stage the hydrogenation of benzene to cyclohexene over the Ru–Zn alloy catalyst can be accomplished with less restriction. In the middle stage of hydrogenation, cyclohexene yield is guaranteed by the seriously restrained reaction kinetics and the adsorption of cyclohexene on the alloy surface.

Usually, the residence time to obtain the highest cyclohexene yield is extended along with the increase in metallic Zn content in the alloy catalyst. In theory, such an increase may eventually quench not only the hydrogenation of cyclohexene but also the partial hydrogenation of benzene to cyclohexene. An optimal metallic Zn content thus is preferred to obtain a satisfied cyclohexene yield within the reasonable reaction time. At present, the optimized composition of Ru–Zn alloy catalyst can only be determined experimentally. However, theoretical calculation in this work still can provide helpful clues for the optimization to the Ru–Zn alloy catalyst.

## 4. Conclusions

By theoretical calculation on the adsorption behavior of cyclohexene on the Ru(0001) surface and Ru–Zn/Ru(0001) surface,

it is found that the presence of Zn atoms leads to a passivation to the surface alloy for the chemisorptions of cyclohexene, and such a passivation nearly covers the whole surface applied in this work. Furthermore, the subsequent cyclohexene hydrogenation on the surface alloy can only be accomplished when the cyclohexene molecules are adsorbed at the specific positions with respect to the location of neighboring Zn atoms. In most cases, the hydrogenation is prohibited due to the repulsion from the Zn atoms to the H atoms participating in the reaction. For the Ru–Zn alloy catalyst applied in the partial hydrogenation of benzene, both the adsorption and the surface hydrogenation of cyclohexene on the catalyst surface are restrained in the middle stage of reaction, which is supposed to be crucial to the improvement of cyclohexene yield. Calculation results also propose an optimal Zn composition in the alloy catalyst to obtain a satisfied cyclohexene yield within a reasonable reaction time.

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