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Discrimination of the roles of $CdSO_4$ and $ZnSO_4$ in liquid phase hydrogenation of benzene to cyclohexene

Jian-Liang Liu [a], Yuan Zhu [a], Jun Liu [a], Yan Pei [a], Zhen Hua Li [a,*], Hui Li [b], He-Xing Li [b], Ming-Hua Qiao [a,*], Kang-Nian Fan [a]

[a] Department of Chemistry and Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Shanghai 200433, PR China
[b] Department of Chemistry, Shanghai Normal University, Shanghai 200234, PR China

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ABSTRACT

$CdSO_4$ and $ZnSO_4$ as co-modifiers of RuLa/SBA-15 lead to improved catalysts for the partial hydrogenation of benzene to cyclohexene. Based on the experimental results and theoretical calculations, it is shown that $CdSO_4$ acts as surface modification, suppressing more the adsorption of cyclohexene than that of benzene, while the function of $ZnSO_4$ is mainly the stabilization of cyclohexene in the liquid phase, accelerating the desorption as well as hindering the re-adsorption of cyclohexene.

1. Introduction

There has been a growing interest in using heterogeneous catalysts for the partial hydrogenation of benzene to cyclohexene, a greener intermediate feedstock than cyclohexane for producing nylons and fine chemicals [1–3]. However, it is thermodynamically difficult to obtain cyclohexene in high selectivity, since the standard free energy change for cyclohexene formation from benzene hydrogenation is $-5.5\ \text{kcal mol}^{-1}$, while that for cyclohexane formation is $-23.4\ \text{kcal mol}^{-1}$. Therefore, it has been a long time that only cyclohexane was obtained during the hydrogenation of benzene [4].

In order to improve the selectivity to cyclohexene, the addition of a modifier to the reaction system (the so-called reaction or process modifier [5]) is indispensable [6,7]. Generally, there are two kinds of reaction modifiers: organic and inorganic. Effective organic modifiers should contain a polar group such as hydroxyl or amine group [8–11]. IR studies revealed the adsorbate–adsorbate interaction between the organic modifier (e.g. ε-caprolactam, glycol, or aliphatic alcohols) and cyclohexene through hydrogen bonding [8,9]. As a consequence, overlapping of π-electrons of the double bond in cyclohexene with d-orbitals of Ru, the most selective catalyst for this reaction, is diminished, and the hydrogen-bonded cyclohexene would desorb at a higher rate than cyclohexene bonded directly to the catalyst. However, since the bonding between organic modifiers and cyclohexene is very weak (enthalpy of hydrogen bonding is about $-1\ \text{kcal mol}^{-1}$), the selectivity to cyclohexene never exceeded 40% when using these organic modifiers.

Inorganic modifiers such as Zn, Fe, Co, Ni, Cd, Ga, and In salts are more effective than organic modifiers [6]. Among them, $ZnSO_4$ has been regarded as the best modifier, and Asahi Chemical has industrialized a process based on Ru as the catalyst and $ZnSO_4$ as the modifier for partial hydrogenation of benzene to cyclohexene [3]. However, there is no consensus on the role of $ZnSO_4$ in improving the selectivity. For example, Fukuoka and coworkers [3,12] attributed the promoting effect of $ZnSO_4$ to the stabilization of the hydrogenated intermediate by forming adduct with cyclohexene, which weakens the adsorption of cyclohexene on Ru and increases the rate of desorption. On the other hand, Struijk et al. [6,13] ascribed the promoting effect of $ZnSO_4$ to its chemisorption on the surface of the Ru catalyst that results in a hydrophilic surface. Thus, the Ru particles are surrounded by a stagnant water layer that impedes the adsorption of H_2 and cyclohexene onto the Ru surface and consequently, slows down the further hydrogenation of cyclohexene. An important reason for such controversy is the poor understanding of the phenomenon due to its unforeseen complexity and to the unavailability of in situ characterization results [5].

Moreover, all published documents have focused on using one inorganic modifier in the partial hydrogenation of benzene to

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* Corresponding authors. Fax: +86 21 65641740.
E-mail addresses: lizhenhua@fudan.edu.cn (Z.H. Li), mhqiao@fudan.edu.cn (M.-H. Qiao).

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cyclohexene. In the present work, we employed for the first time a combination of two inorganic modifiers, $CdSO_4$ and $ZnSO_4$, for the target reaction, and found that two modifiers performed much better than either of them alone. In order to elucidate the respective role of $CdSO_4$ and $ZnSO_4$ in the reaction, we fell to theoretical calculation to obtain the information about the interactions of Cd^{2+} and Zn^{2+} ions with benzene and cyclohexene. Based on the experimental data and theoretical results, the modification effects of $CdSO_4$ and $ZnSO_4$ on selectivity enhancement were discriminated.

2. Experimental methods

2.1. Catalyst preparation

The mesoporous siliceous SBA-15 was synthesized according to the procedure proposed by Zhao et al. [14]. The catalyst was prepared by a “two solvents” method [15,16]. Namely, 30 ml of cyclohexane was added to 1.0 g of SBA-15 under stirring at 298 K. After all SBA-15 was well dispersed, 3.0 ml of 0.04 g Ru per ml of $RuCl_3$ solution containing 0.40 g $La(NO_3)_3 \cdot 6H_2O$ was added drop by drop with stirring. The supernatant was decanted, and the solid residue was dried at 373 K overnight, before it was reduced by 5 vol.% H_2/Ar gas at 573 K for 4 h at a ramping rate of 2 K min^{-1}. This as-prepared catalyst was designated RuLa/SBA-15.

2.2. Activity testing

Liquid phase hydrogenation of benzene was carried out in a 500 ml stainless steel autoclave with a mechanical stirrer. The autoclave was charged with 100 ml of distilled water containing a desired amount of the modifier(s), 1.0 g of catalyst, and 50 ml of benzene, then sealed and purged with H_2 for 4 times to exclude air. The reaction was performed at a reaction temperature of 413 K, H_2 pressure of 4.0 MPa, and stirring rate of 1000 rpm to exclude the diffusion effect. The reaction process was monitored by gas chromatographic analysis using a PEG-20 M packed column and a thermal conductivity detector (TCD).

2.3. Theoretical calculation

The B3PW91 density functional method [17–19] in conjunction with the 6-31+G(d) basis set was used to optimize the complexes formed between benzene or cyclohexene and the metal ions of $CdSO_4$ and $ZnSO_4$ to simulate the interaction between the reactant or intermediate with the metal ions in the liquid phase during the hydrogenation of benzene to cyclohexene. We have considered the interaction of both bare and hydrated metal ions with benzene and cyclohexene. Two possible binding configurations have been considered: binding of one bare or hydrated metal ion to one and two benzene or cyclohexene molecules. The calculations were all performed with the Gaussian 03 software package [20]. Default convergence criteria were used for the geometry optimization. Vibrational frequency analyses were performed for the optimized geometries.

3. Results

3.1. The modification effect of $CdSO_4$

Although the effect of the concentration of $ZnSO_4$ on the performance of Ru catalysts has been extensively investigated in liquid phase hydrogenation of benzene to cyclohexene [6,15,16,21], only one work on $CdSO_4$ was reported, probably due to its inferior modification effect to that of $ZnSO_4$ [6]. As summarized in Table 1, the reaction proceeded very fast in the absence of $CdSO_4$. The conversion of benzene reached 76% within 3 min. However, the maximum yield of cyclohexene was only 7% with the corresponding selectivity to cyclohexene of 9%. With the increase of the concentration of $CdSO_4$ to 1.56×10^{-3} M, cyclohexene reached a maximum yield of 28%. For comparison, by using Ru black as the catalyst, Struijk et al. found that the yield of cyclohexene maximized at 1.48×10^{-3} M of $CdSO_4$ [6], which is in good agreement with our observation, although their yield was only 16.9% and decreased more drastically than our case on both the lower and higher concentration sides of $CdSO_4$. At higher concentrations of $CdSO_4$, the reaction slowed down further, and the maximum yield of cyclohexene declined continuously (Table 1). At 2.34×10^{-3} M of $CdSO_4$, the reaction rate was less than 1/15 of that without $CdSO_4$, and the yield of cyclohexene was decreased to 15%.

Table 1
Results of the hydrogenation of benzene over the RuLa/SBA-15 catalyst with different concentrations of $CdSO_4$.[a]

$CdSO_4$ (10^{-3} M)	Conversion[b] (%)	Selectivity[b] (%)	Yield[b] (%)	Time[b] (min)
0	76	9	7	3
1.17	82	32	26	5
1.56	84	33	28	6
1.95	76	35	27	11
2.34	55	27	15	45

[a] Reaction conditions: 1.0 g of catalyst, 50 ml of benzene, 100 ml of H_2O, temperature of 413 K, H_2 pressure of 4.0 MPa, stirring rate of 1000 rpm.

[b] Values recorded at the maximum yield of cyclohexene.

3.2. The synergistic effect of $CdSO_4$ and $ZnSO_4$

Since the addition of 1.56×10^{-3} M of $CdSO_4$ afforded the optimal modification effect, and $ZnSO_4$ has been testified as the most effective modifier for this reaction [3,6], we additionally modified the reaction system containing $CdSO_4$ with $ZnSO_4$ aiming to further improve the selectivity to cyclohexene. As shown by the data given in Table 2, in the presence of 1.56×10^{-3} M of $CdSO_4$, an increment of the concentration of $ZnSO_4$ from zero to 0.42 M resulted in an increase of the selectivity to cyclohexene from 33% to 69% measured at the maximum yield of cyclohexene. Accordingly, the yield of cyclohexene was increased to 57%, which is among the best results reported so far. Further increasing of the concentration of $ZnSO_4$ to 0.56 M led to lower selectivity and yield of cyclohexene. Fig. 1 presents the courses of the hydrogenation of benzene in the presence of 1.56×10^{-3} M of $CdSO_4$ alone and a combination of 1.56×10^{-3} M of $CdSO_4$ and 0.42 M of $ZnSO_4$ for comparison.

In addition, we optimized the concentration of $ZnSO_4$ as the sole modifier under the same reaction condition over the same catalyst. The optimal concentration of $ZnSO_4$ is also 0.42 M. As indicated in entry 7 of Table 2, this concentration of $ZnSO_4$ afforded a maximum yield of cyclohexene of 39%, and the corresponding selectivity to cyclohexene is 51%. It should be mentioned that the optimal concentration of $ZnSO_4$ is two orders of magnitude higher than that of $CdSO_4$. In addition, $ZnSO_4$ has a much less remarkable negative effect on the hydrogenation activity. In the presence of 0.42 M of $ZnSO_4$, the conversion of benzene is 76% within 10 min. A comparable activity was observed using only 1.95×10^{-3} M of $CdSO_4$ as the modifier (entry 4, Table 1).

3.3. Interactions of Cd^{2+} and Zn^{2+} ions with benzene and cyclohexene

To gain a better insight into the roles of Cd^{2+} and Zn^{2+} ions in liquid phase hydrogenation of benzene to cyclohexene, we fell to theoretical calculation to investigate the interactions of Cd^{2+} and Zn^{2+} ions with benzene and cyclohexene molecules. The optimized

Table 2
Results of the hydrogenation of benzene over the RuLa/SBA-15 catalyst at different concentrations of $ZnSO_4$.[a]

$ZnSO_4$ (M)	Conversion[b] (%)	Selectivity[b] (%)	Yield[b] (%)	Time[b] (min)	$x_{Cd^{2+}}$[d] (%)	$x_{Zn^{2+}}$[d] (%)
0	84	33	28	5	–	–
0.14	77	59	45	28	13	0.23
0.28	81	64	52	32	11	0.36
0.42	82	69	57	34	12	0.54
0.56	83	64	53	39	11	0.58
0.14[c]	72	41	30	9	–	–
0.42[c]	76	51	39	10	–	–

[a] Reaction conditions: 1.0 g of catalyst, 50 ml of benzene, 100 ml of H_2O, temperature of 413 K, H_2 pressure of 4.0 MPa, stirring rate of 1000 rpm, and C_{CdSO_4} of 1.56×10^{-3} M.

[b] Values recorded at the maximum yield of cyclohexene.

[c] Without $CdSO_4$.

[d] x = (the amount of cation in the catalyst)/(the amount of cation added in the aqueous phase) × 100%. The catalysts after reaction were washed with water for 6 times before being subjected to the elemental analysis.

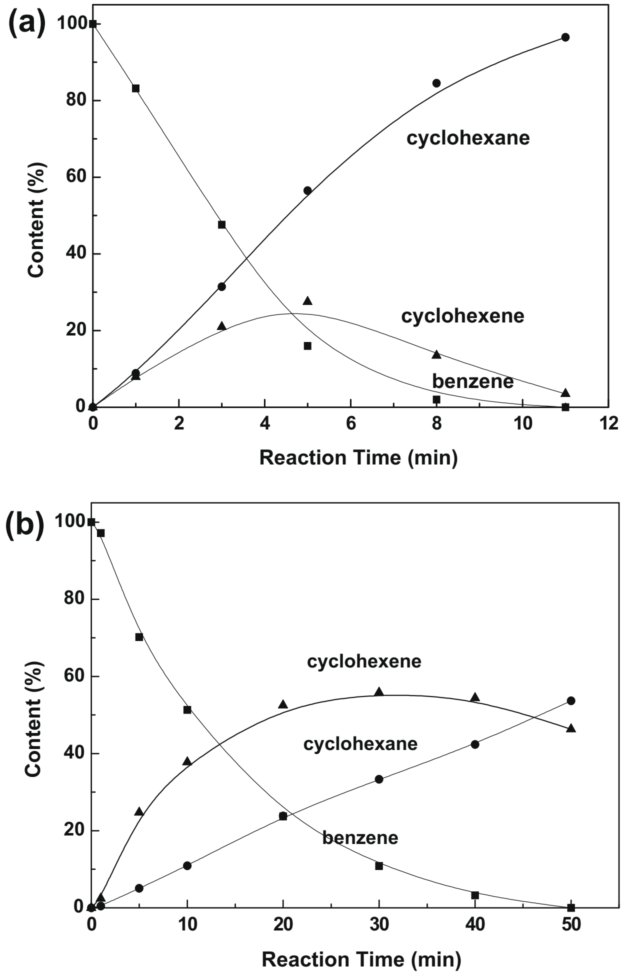

Fig. 1. The reaction course of benzene hydrogenation over the RuLa/SBA-15 catalyst. Reaction conditions: 1.0 g of catalyst, 100 ml of H_2O, 50 ml of benzene, T of 413 K, P of 4.0 MPa, stirring rate of 1000 rpm, (a) 1.56×10^{-3} M $CdSO_4$, (b) 1.56×10^{-3} M $CdSO_4$ and 0.42 M $ZnSO_4$.

geometries of the complexes between one bare metal cation and one and two organic molecules are illustrated in Fig. 2. In the complexes formed by the bare metal cation and one benzene molecule, both Cd^{2+} and Zn^{2+} ions sit above the ring plane and both the complexes have a C_{6v} symmetry. On the other hand, Cd^{2+} and Zn^{2+} ions have different bonding configurations when binding to two benzene molecules. The Cd^{2+} ion bonds to just one carbon atom of each benzene molecule, while the Zn^{2+} ion bonds to two carbon atoms of each benzene molecule. When binding to cyclohexene, both cations form normal cation-π bonding with the cyclohexene molecule.

The formation energies of the complexes, i.e. the relative potential energies between the complexes and their corresponding components (cation plus benzene or cyclohexene) are presented in Table 3. Both benzene and cyclohexene can form stable complexes with Cd^{2+} and Zn^{2+} ions, and one important conclusion that can be drawn from the data given in Table 3 is that the Zn^{2+} ion binds more tightly with benzene and cyclohexene than the Cd^{2+} ion. The formation energies of the complexes of the Zn^{2+} ion formed with one and two benzene or cyclohexene molecules are about 30–50 kcal mol^{-1} more negative than those of the Cd^{2+} ion.

We have also explicitly taken the solvent effect of water into consideration and optimized the geometries of the complexes formed by one hydrated metal cation and one and two benzene or cyclohexene molecules. Fig. 3 illustrates the optimized geometries, and Table 4 presents the formation energies of the complexes formed by the hydrated metal cations. The formation energies are defined as the energy changes to form the complexes from the $M(H_2O)_6^{2+}$ (M = Zn, Cd) ions, since the first hydration shell of Cd^{2+} and Zn^{2+} contains six water molecules [22,23]. The results of the complexes formed between one hydrated metal cation and two benzene or cyclohexene molecules are not shown here, because their formation energies are positive. It is found that when including the effect of water, the binding energies of the complexes between the hydrated metal cations and one benzene or cyclohexene molecule are much less negative than those without water. However, the conclusion is still valid that the hydrated Zn^{2+} ion binds more tightly with benzene and cyclohexene than the hydrated Cd^{2+} ion.

4. Discussion

The theoretical calculation results have two important implications for the understanding of the roles of $CdSO_4$ and $ZnSO_4$ in partial hydrogenation of benzene to cyclohexene. (1) The Cd^{2+} ion binds more weakly with benzene than the Zn^{2+} ion. Therefore, a more drastic decrement in the hydrogenation activity when $CdSO_4$ was used as the modifier cannot be attributed to a stronger interaction of the Cd^{2+} ion with benzene that can impede the adsorption of benzene on the catalyst. (2) The Zn^{2+} ion forms a more stable complex with cyclohexene than the Cd^{2+} ion. Such a stabilization effect can accelerate the desorption of the intermediate product cyclohexene from the catalyst surface, or retard the re-adsorption of the desorbed cyclohexene, thus improving the selectivity to cyclohexene [3]. As a result, it is unlikely that the selectivity enhancement at 1.56×10^{-3} M of $CdSO_4$ (entry 3, Table 1) should be mainly attributed to such a stabilization effect, because a com-

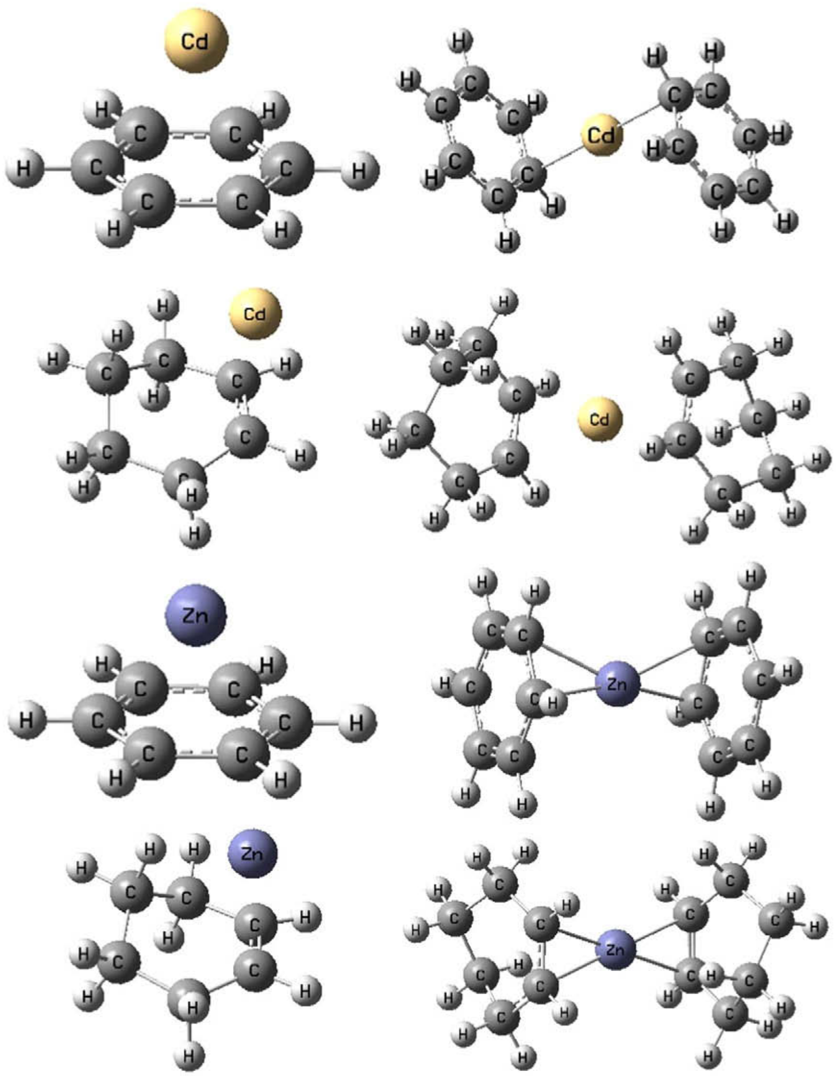

Fig. 2. Optimized geometries of the complexes formed by bare Cd^{2+} and Zn^{2+} ions. Left: binding of metal cation to one benzene or cyclohexene molecule; Right: binding of metal cation to two benzene or cyclohexene molecules.

Table 3

Formation energies (kcal mol^{-1}) of the complexes formed between Cd^{2+} and Zn^{2+} ions and benzene or cyclohexene, where a more negative value indicates that the corresponding complex is more stable.[a]

Ligand	Cd^{2+}	Zn^{2+}
Benzene	−125.9	−165.9
$(Benzene)_2$	−205.0	−250.8
Cyclohexene	−140.6	−174.3
$(Cyclohexene)_2$	−212.6	−256.1

[a] Zero-point vibrational energy corrected.

parable selectivity enhancement was found at as high as 0.14 M of $ZnSO_4$ (entry 6, Table 2) that is more efficient in stabilizing cyclohexene as predicted by theoretical calculation.

On the other hand, it has been proposed that the water layer surrounding the catalyst can impede the re-adsorption of cyclohexene, so the influence of the metal cation on the hydrophilicity of the catalyst also affects the selectivity to cyclohexene [6,13]. Although the effect of the adsorbed Zn^{2+} and Cd^{2+} ions on the hydrophilicity of the catalyst is not known exactly due to complexity of the practical catalyst, our theoretical results suggest that the binding energy between the Zn^{2+} ion and six water molecules is more negative than that of the Cd^{2+} ion (−56.8 vs. −48.0 kcal mol^{-1}). This indicates that the Zn^{2+} ion, when adsorbed on the catalyst, will be more effective in improving the hydrophilicity of the catalyst. If such an effect dominates the selectivity enhancement in the present case, a concentration of $ZnSO_4$ lower than that of $CdSO_4$ would be expected to achieve a similar selectivity to cyclohexene, which is in sharp contrast to the experimental results reported in Tables 1 and 2.

These findings prompt us to conclude that $CdSO_4$ tends to influence the selectivity via directly modifying the active sites of the catalyst, whereas $ZnSO_4$ plays a more effective role in stabilizing the intermediate product cyclohexene in the liquid phase, while affecting less markedly the activity of the catalyst even at much higher concentrations. The synergistic effect of these two modifiers results in a higher selectivity to cyclohexene than using either of them alone. Moreover, elemental analysis data show that more than 10% of the initial Cd^{2+} ions remain on the used catalyst after being separated and washed with water for 6 times (Table 2). When the concentration of $ZnSO_4$ was increased from 0.14 to 0.56 M, the amount of Cd^{2+} ions left on the catalyst maintained nearly unaltered, implying that Zn^{2+} ions compete less favorably than Cd^{2+} ions with the active sites. According to the "Maxted rule", electrons of cations that have a fully or partially occupied

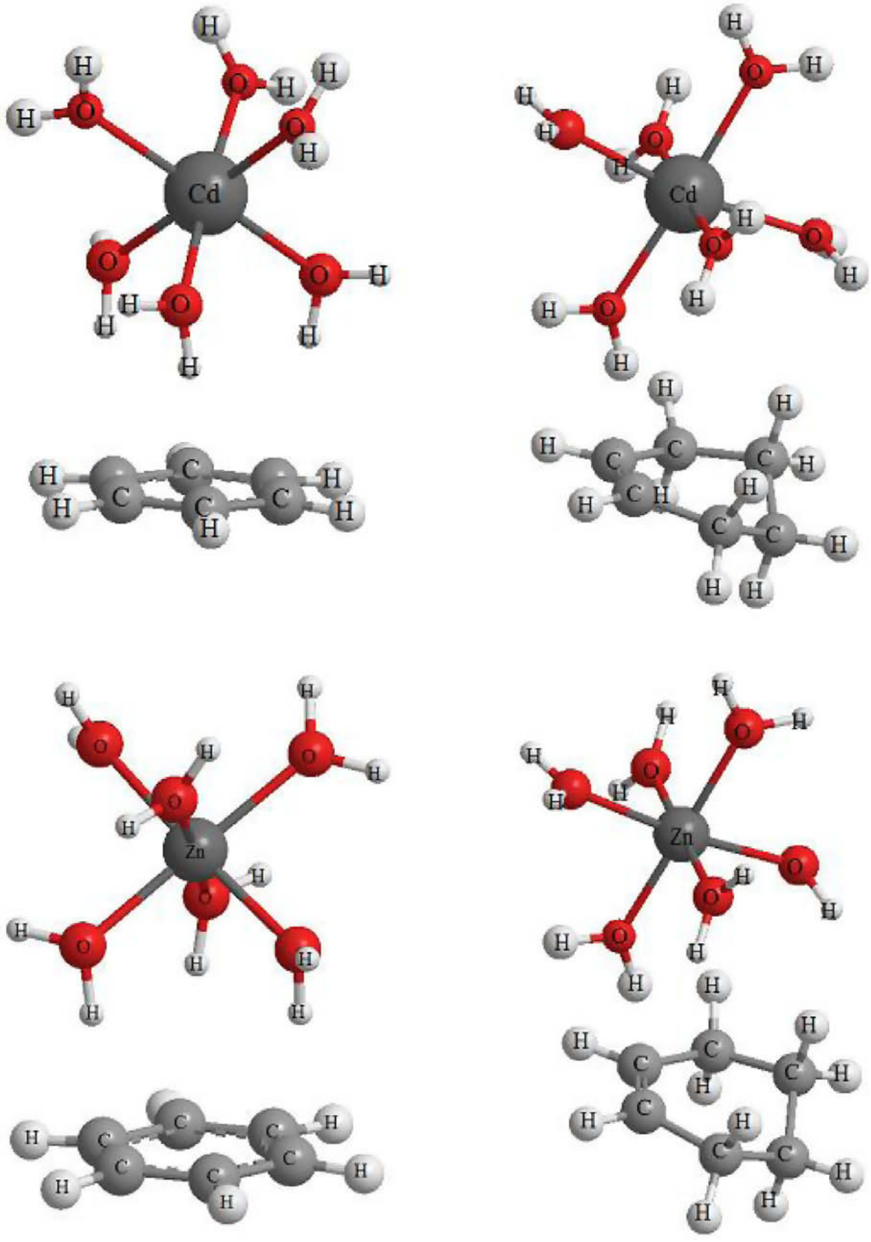

Fig. 3. Optimized geometries of the complexes formed by hydrated Cd^{2+} and Zn^{2+} ions. Left: binding of the hydrated metal cation to one benzene molecule; Right: binding of the hydrated metal cation to one cyclohexene molecule.

Table 4
Formation energies ($kcal\,mol^{-1}$) of the complexes formed by $Cd(H_2O)_6^{2+}$ and $Zn(H_2O)_6^{2+}$ ions and benzene or cyclohexene, where a more negative value indicates that the corresponding complex is more stable.[a]

Ligand	$Cd(H_2O)_6^{2+}$	$Zn(H_2O)_6^{2+}$
Benzene	−13.8	−15.7
Cyclohexene	−12.7	−13.7

[a] Zero-point vibrational energy corrected.

4d shell are more weakly bound to the nucleus of the cation than electrons of cations that have a 3d shell [24]. Therefore, Cd^{2+} ions with a fully occupied 4d shell have a higher electron-donating power in the direction of the metal surface than Zn^{2+} ions with a fully occupied 3d shell, resulting in a stronger cation bonding [6]. Godard et al. [25] studied the adsorption of Cd^{2+} ions on a Ni surface in an aqueous solution, and found that the Cd^{2+} ion deposition is thermodynamically driven by the formation of Cd–Ni bond. When Ni is covered by a monolayer of Cd, the Ni surface is not accessible by the reactant anymore. The same is true for the present case. Table 1 reveals the progressive deactivation of the RuLa/SBA-15 catalyst with the increment of the concentration of $CdSO_4$. At even higher concentration of $CdSO_4$, the complete deactivation of the catalyst is expected.

However, the decrement in the hydrogenation activity after the adsorption of Cd^{2+} ions cannot be simply attributed to the physical blocking of the active sites by the catalytically inactive Cd^{2+} ions. It is known that the adsorption of benzene on Ru surface requires more contiguous active sites than that of cyclohexene [26,27]. Thus, the site blocking effect would influence more remarkably the adsorption and hydrogenation of benzene than that of cyclohexene, which should lower the selectivity to cyclohexene. This is not consistent with the results in Table 1, which shows that the decreased hydrogenation activity after the modification by Cd^{2+} ions is accompanied firstly by an improved selectivity to cyclohexene. Based on DFT calculations, He et al. found that the modification of the Ru(0 0 0 1) surface by metal atom suppresses simultaneously the adsorption of benzene and cyclohexene, with the latter being more severely suppressed [28]. Following this result and assuming that the adsorption of benzene and cyclohexene determines their respective hydrogenation activities, it is a natural extrapolation that after the modification of Cd^{2+} ions on the catalyst, the conversion of benzene is lowered, while the selectivity to cyclohexene is improved. Similar effect is known in the partial hydrogenation of alkynes to alkenes. The selectivity for acetylene hydrogenation in a acetylene/ethylene mixture can be enhanced up to 100% over supported Pd catalysts promoted with Pb^{2+}, Zn^{2+}, Cd^{2+}, or Hg^{2+} salts, better known as Lindlar catalysts [6]. A plausible explanation for the high selectivity is that due to the presence of these metal cations on the Pd surface, the adsorption enthalpy of ethylene is reduced to a greater extent than that of acetylene [29].

5. Conclusions

The synergistic effect of two metal cations on selective hydrogenation has been seldom investigated and interpreted. We found that $CdSO_4$ and $ZnSO_4$ as co-modifiers are highly efficient in the partial hydrogenation of benzene to cyclohexene. $CdSO_4$ plays a more important role in surface modification, suppressing more the adsorption of cyclohexene than that of benzene, while the function of $ZnSO_4$ is mainly to stabilize cyclohexene in the liquid phase, accelerating the desorption as well as hindering the re-adsorption of cyclohexene. This finding may open a new avenue for selectivity enhancement for other hydrogenation reactions.

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