



# Liquid-phase selective hydrogenation of benzene to cyclohexene on Ru/Al<sub>2</sub>O<sub>3</sub>–ZrO<sub>2</sub>/cordierite monolithic catalysts

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## ABSTRACT

Monolithic catalysts, Ru/Al<sub>2</sub>O<sub>3</sub>–ZrO<sub>2</sub>/cordierite, were prepared by dipcoating and impregnation for liquid-phase selective hydrogenation of benzene to cyclohexene in a continuous fixed bed reactor. Ru/Al<sub>2</sub>O<sub>3</sub>–ZrO<sub>2</sub>/cordierite showed excellent catalytic performance due to the high specific surface area and the large pores of Al<sub>2</sub>O<sub>3</sub>–ZrO<sub>2</sub> support. The Zr/Al ratio was optimized to be 0.116 and the excessive amount of ZrO<sub>2</sub> resulted in a decreased specific surface area of the Al<sub>2</sub>O<sub>3</sub>–ZrO<sub>2</sub> washcoating layer. The preferable calcination temperature is 1373 K for Al<sub>2</sub>O<sub>3</sub>–ZrO<sub>2</sub> support, at which suitable BET surface area and pore size distribution could be obtained. It was also found that appropriate ratio of Zn/Ru was essential to obtain high selectivity. Additionally, compared to the powder catalysts used in the slurry reactor, the monolithic catalysts exhibited much higher activity regarding the yield of cyclohexene and cyclohexane.

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## 1. Introduction

Cyclohexene is an intermediate in the production of cyclohexanol, raw materials for the production of adipic acid and caprolactane, which in turn can be used in polyamide industry [1]. Selective hydrogenation of benzene to cyclohexene (SHBC) has attracted much attention during the past decades since it provides a more efficient and economical route for the production of adipic acid and caprolactane than that via cyclohexane [2,3]. Different catalysts [4–16] have been proposed for the reaction, among which nano-scale ruthenium-based catalysts suspended in an aqueous solution of ZnSO<sub>4</sub> is one of the best. It was suggested that water can displace adsorbed cyclohexene thus lowering the rate of cyclohexene hydrogenation [7]. On the other hand, catalytic systems without ZnSO<sub>4</sub> have also been developed to prevent the corrosion of the reactor. Silveira et al. [17] reported a nano-scale ruthenium catalyst in imidazolium ionic liquid yield 2% of cyclohexene. Spinace et al. [18] and Mazziari et al. [19] found that some polar organic additives, such as ethanol, ethylene glycol and glycerol, made the ruthenium catalyst hydrophilic and prompted the cyclohexene des-

orption. Fan et al. [20] prepared a bimetallic catalyst RuCoB/γ-Al<sub>2</sub>O<sub>3</sub> by reduction impregnation, on which the maximum cyclohexene yield of 28.8% was reached without any additive during the reaction. Notably, most of the reactions were conducted in a tetra-phase slurry tank reactor with strong stirring and high pressure. This configuration can help the catalyst dispersed in the slurry and tackle the external mass transfer of benzene and hydrogen, leading to the high yield of cyclohexene [10,12,14].

Recently, we reported on a novel monolithic catalyst and fixed bed reaction system and their excellent catalytic performance in SHBC [21,22]. The problems existing in the stirred batch reactor such as the separation of ultra-fine powder catalyst from the liquid products, severe agitation, and the difficulty to scale up, could be solved easily in the novel integrated monolithic fixed bed reactor (MFBR) system [23,24]. We have previously shown that a high cyclohexene yield of 30% could be obtained on Ru/Al<sub>2</sub>O<sub>3</sub>–ZrO<sub>2</sub>/cordierite catalysts [21]. As a continuing investigation, in this work, Ru/Al<sub>2</sub>O<sub>3</sub>–ZrO<sub>2</sub>/cordierite monolithic catalysts are prepared and characterized. We have also evaluated the catalytic performances on the SHBC in a MFBR system.

## 2. Experimental

### 2.1. Catalyst preparation

Cordierite monolith substrates (400 cells per square inch (cps), diameter = 10 mm, length = 22 mm) were first coated with

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**Table 1**  
Surface areas, pore volumes and average diameters of the washcoats on the cordierite monolith calcined at 1373 K.

Sample	Pore size (nm)	Surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Volume ratio of 1–4 nm	Volume ratio of 7–20 nm
Al <sub>2</sub> O <sub>3</sub>	15.1	32	0.12	10%	27%
ZrO <sub>2</sub>	11.1	3.6	0.01	–	–
Al <sub>2</sub> O <sub>3</sub> –ZrO <sub>2</sub>	8.8	90	0.2	19%	42%

Al<sub>2</sub>O<sub>3</sub>–ZrO<sub>2</sub> layer using a dipcoating method [25] in an Al<sub>2</sub>O<sub>3</sub>–ZrO<sub>2</sub> slurry. Various thicknesses of Al<sub>2</sub>O<sub>3</sub>–ZrO<sub>2</sub> on the substrates were achieved by multi-times dipcoating. The coated cordierite monoliths were calcined at temperatures ranges from 1173 to 1473 K and were impregnated in an aqueous solution of RuCl<sub>3</sub> followed by drying in a microwave for 3 min and calcined in static air at 573 K for 2 h. The concentration of the RuCl<sub>3</sub> solution was varied to obtain different ruthenium loading. If not specified, the loadings of the washcoating layer and the ruthenium were 5 and 0.3 wt% for all the catalysts. The catalyst was named as CMZAR.

For a comparison purpose, two catalysts were prepared by the same method mentioned above except that Al<sub>2</sub>O<sub>3</sub>–ZrO<sub>2</sub> slurry was replaced by the alumina slurry or zirconia slurry, respectively. The as-prepared cordierite monolithic catalysts were denoted as CMAR and CMZR, respectively, for the alumina coated monolithic catalyst and the zirconia coated monolithic catalyst.

The alumina slurry was prepared by wet-milling the mixture of Al<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O, γ-Al<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>·3H<sub>2</sub>O and Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O in a HNO<sub>3</sub> aqueous solution with a planetary mixer (BM-BP, Nanjing University Instrument Plant) at room temperature for 18 h. The pH of the slurries was adjusted to 4.0 with HNO<sub>3</sub>. The Al<sub>2</sub>O<sub>3</sub>–ZrO<sub>2</sub> slurry was prepared by the same method except certain amount of Zr(NO<sub>3</sub>)<sub>2</sub> was added. The zirconia slurry was prepared by wet-milling of ZrO<sub>2</sub> and Zr(NO<sub>3</sub>)<sub>2</sub> in HNO<sub>3</sub>.

## 2.2. Catalyst characterization

The BET surface areas and average pore diameter of the samples were measured based on nitrogen adsorption measurements at 77 K with a Micromeritics ASAP 2400 instrument. The values obtained exclusively reflect the properties of the washcoat.

XRD data were recorded to examine the bulk structure of the samples by a Rigaku D/Max-2500 XRD diffractometer with Cu Kα radiation.

## 2.3. Catalyst test

Selective hydrogenation of benzene to cyclohexene was carried out in a continuous-flow fix-bed reactor in middle of which monolithic catalyst was placed. A 10-h reduction process was conducted at 3.0 MPa and 473 K after air was flushed out using pure hydrogen. Subsequently, 2 h of pretreatment with an aqueous solution of ZnSO<sub>4</sub> at the flow rate of 1 ml/min was carried out in the hydrogen flow at 423 K. Then, benzene (>99.9%), ZnSO<sub>4</sub> solution (0.5 wt% when not mentioned) and hydrogen were charged in from the top of the reactor through the high pressure pump and mass flow controller. The reaction was carried out at 3.0 MPa and 423 K. Samples were withdrawn at intervals and analyzed by GC-FID. Conversion of benzene (C), selectivity (S) and yield (Y) of cyclohexene were calculated according to the following equations:

$$C = \frac{\text{mole of reacted benzene}}{\text{mole of initial benzene}} \times 100$$

$$S = \frac{\text{mole of cyclohexene formed}}{\text{mole of reacted benzene}} \times 100$$

$$Y = \frac{\text{mole of cyclohexene formed}}{\text{mole of initial benzene}} \times 100$$

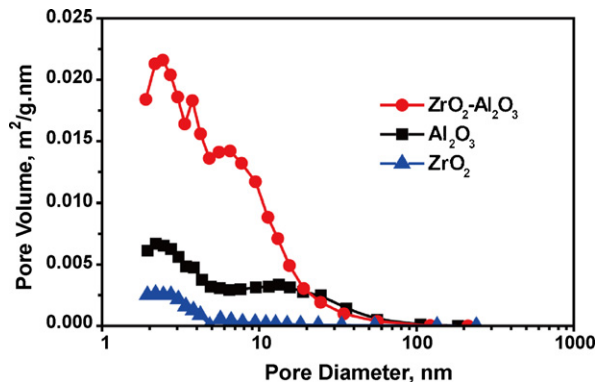


Fig. 1. Pore size distribution of different washcoats.

## 3. Results and discussion

### 3.1. Characterization

#### 3.1.1. BET

The physical adsorption characters of Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>–ZrO<sub>2</sub> were examined by BET analysis. As shown in Table 1, the specific surface area of Al<sub>2</sub>O<sub>3</sub>–ZrO<sub>2</sub> is much higher than those of Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub>. Although the average pore diameter of Al<sub>2</sub>O<sub>3</sub>–ZrO<sub>2</sub> was lower than that of Al<sub>2</sub>O<sub>3</sub>, the pore volumes increased significantly in the ranges of 1–4 nm and of 7–20 nm as shown in Fig. 1. This could be due to the enhanced resistance to sintering and the grain growth of Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub> with the addition of ZrO<sub>2</sub> into Al<sub>2</sub>O<sub>3</sub> [27].

Various Al<sub>2</sub>O<sub>3</sub>–ZrO<sub>2</sub> slurries were also prepared with different Zr/Al ratio and characterized by BET and the results are listed in Table 2. Briefly speaking, the BET specific surface area increased with the increase in Zr/Al ratio and decreased sharply when the Zr/Al exceeds 0.116. This threshold ratio (0.116) could be the preferential choice to achieve highest BET specific surface area. Additionally, it indicated that excess amount of ZrO<sub>2</sub> could not enhance the resistance to the sintering of Al<sub>2</sub>O<sub>3</sub>, but only gave a negative effect on the specific surface areas of Al<sub>2</sub>O<sub>3</sub>–ZrO<sub>2</sub>.

#### 3.1.2. XRD

Fig. 2 shows XRD patterns of Al<sub>2</sub>O<sub>3</sub>–ZrO<sub>2</sub> samples with different Zr/Al. When the Zr/Al increased from 0.058 to 0.116, the characteristic peaks for tetra-ZrO<sub>2</sub> and mono-ZrO<sub>2</sub> increased, while those for α-Al<sub>2</sub>O<sub>3</sub> decreased significantly. Moreover, other types of Al<sub>2</sub>O<sub>3</sub> were not found. Upon further increasing Zr/Al, few changes were

**Table 2**

Surface areas, pore volumes and average diameters of Al<sub>2</sub>O<sub>3</sub>–ZrO<sub>2</sub> with different Zr/Al ratio calculated at 1373 K.

Zr/Al (mol)	BET (m <sup>2</sup> /g)	Pore diameter (Å)	Pore volume (cm <sup>3</sup> /g)
0	32	15.1	0.12
0.058	38	12.95	0.122
0.116	90	8.86	0.200
0.231	23	13.89	0.080
0.417	20	10.29	0.051

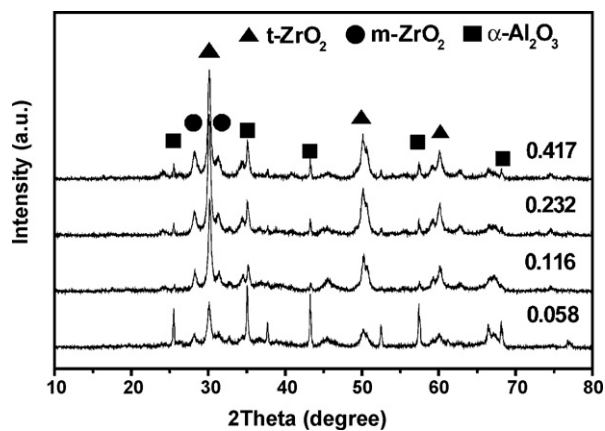


Fig. 2. XRD patterns of  $\text{Al}_2\text{O}_3\text{-ZrO}_2$  with different Zr/Al.

found in the patterns of both  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$  since, as mentioned above, certain amount  $\text{ZrO}_2$  could increase the transformation temperature of the  $\text{Al}_2\text{O}_3$ , but excess amount of  $\text{ZrO}_2$  gave no further influence on the crystal structure.

### 3.2. Performances of the catalyst with different washcoating layer

A brief comparison between the catalyst prepared with  $\text{Al}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3\text{-ZrO}_2$  as the washcoating layer has been reported in the earlier work [21]. It was pointed out that high BET specific surface area of  $\text{Al}_2\text{O}_3\text{-ZrO}_2$  would benefit the dispersion of Ru, providing more active sites for the hydrogenation. In this section, we attempt to provide a more deep investigation on catalysts with different washcoating layer. As shown in Fig. 3, all of three catalysts showed the similar selectivity to cyclohexene, while the conversion of benzene on the catalyst CMZAR was much higher than those on CMAR

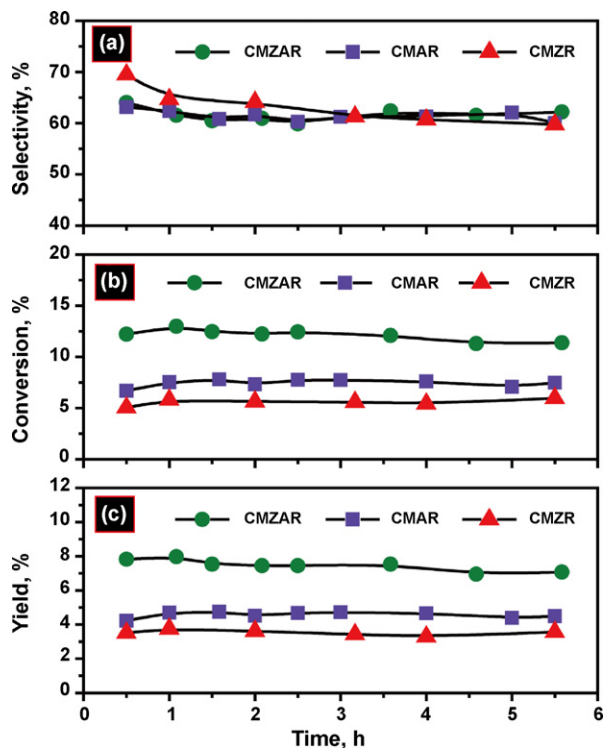


Fig. 3. Catalytic performance of different monolithic catalysts for SHBC. Reaction conditions:  $\text{H}_2/\text{benzene} = 2$  (mol/mol),  $\text{H}_2\text{O}/\text{benzene} = 1$  (v/v),  $P = 3.0$  MPa,  $T = 423$  K, catalyst amount = 3.6 ml and LHSV =  $4\text{ h}^{-1}$ .

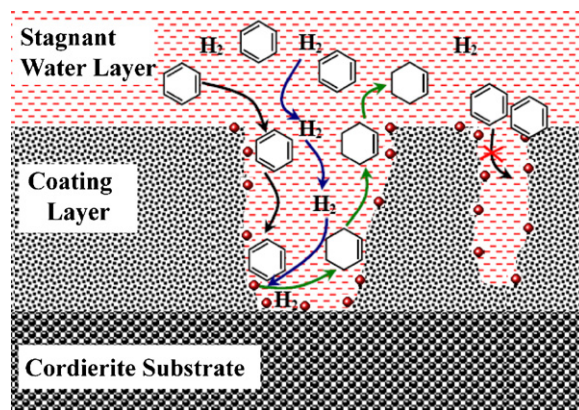


Fig. 4. Schematic diagram of the SHBC on the monolithic catalyst.

and CMZR. Although the conversion on CMZAR was very high and the average pore diameter of the washcoating layer was smaller than the other two catalysts, the selectivity did not decrease much as imagine. The remarkable increase of the pore volume at the range of 7–20 nm in pore diameter was considered as dominant reason for the high selectivity, since the diffusion of cyclohexene could be much easier in the large pores so that the consecutive hydrogenation was prevented. However, small pores (e.g. 1–4 nm) in the catalyst, which were unfavorable for the desorption and diffusion of cyclohexene, could not be fully utilized during the reaction because they can be choked up easily [26]. Therefore, CMZAR showed the highest cyclohexene yield in the SHBC. The schematic diagram of the SHBC on the monolithic catalyst was illustrated in Fig. 4.

### 3.3. Effect of the Zr/Al ratio

Fig. 5 shows the performances of catalysts with different Zr/Al ratio. The conversion of benzene increased from 7.4 to 12.1% with Zr/Al increased from 0 to 0.116, and then decreased to 6.7% at a Zr/Al ratio of 0.417. Note the results are well agreed with the change of the BET surface area mentioned above. Therefore, high BET surface area of the washcoating layer could benefit the high activity of the catalyst.

### 3.4. Effect of the calcination temperature

Since the specific surface area and pore distribution of the support are influenced significantly by calcination temperature [27], the effect of the calcination temperature of the  $\text{Al}_2\text{O}_3\text{-ZrO}_2$  support

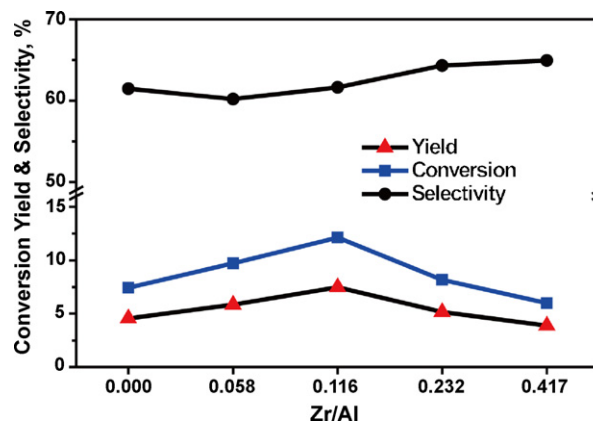


Fig. 5. Catalytic performance of CMZAR with different Zr/Al ratios. Reaction conditions:  $\text{H}_2/\text{benzene} = 2$  (mol/mol),  $\text{H}_2\text{O}/\text{benzene} = 1$  (v/v),  $P = 3.0$  MPa,  $T = 423$  K, catalyst amount = 3.6 ml and LHSV =  $4\text{ h}^{-1}$ .

**Table 3**  
Catalytic performance of monolithic catalyst with Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> washcoat calcined at different temperature.

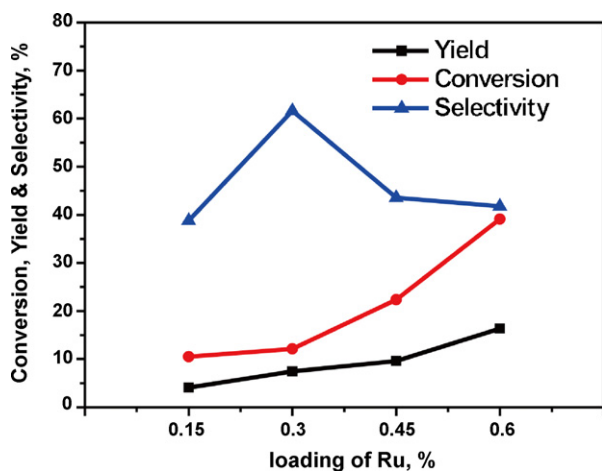
Temperature (K)	Yield (%)	Conversion (%)	Selectivity (%)
1273	6.7	13	52
1373	7.5	12	62
1473	4.6	7	68

Reaction conditions: H<sub>2</sub>/benzene = 2 (mol/mol), H<sub>2</sub>O/benzene = 1 (v/v), P = 3.0 MPa, T = 423 K, catalyst amount = 3.6 ml and LHSV = 4 h<sup>-1</sup>.

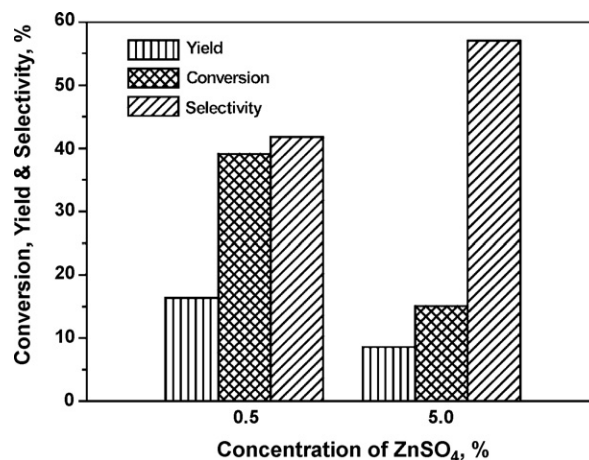
on the catalytic performances was studied. As shown in Table 3, conversion of benzene decreased with an increase in the calcinations temperature. The cyclohexene selectivity showed a remarkable increase from 52 to 68% when the temperature increased from 1273 to 1473 K. The preferential calcination temperature was about 1373 K based on the highest cyclohexene yield. The higher temperature could have a beneficial effect on the structure of ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> compound, but serious sintering would possibly happen on the support at the too high temperature, leading to the deterioration of catalytic performance.

### 3.5. Effect of ruthenium loading

Several monolithic catalysts Ru/Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>/cordierite with ruthenium loadings of 0.15–0.6% were prepared and examined in benzene hydrogenation. As shown in Fig. 6, conversion of benzene increased linearly with an increase in ruthenium loading from 0.15 to 0.6%, while the selectivity increased from 39 to 62% and then decreases to 41% at a ruthenium loading of 0.6%. Though the highest cyclohexene selectivity was reached at a ruthenium loading of about 0.3%, we need to also consider the yield from the industry viewpoint. Therefore, a monolithic catalyst with a ruthenium loading of 0.6% was used in the hydrogenation of benzene while the concentration of ZnSO<sub>4</sub> in the aqueous solution was increased to 5%. Indeed, as shown in Fig. 7, selectivity increased greatly with increasing the ZnSO<sub>4</sub> concentration, which indicates that appropriate Zn/Ru was necessary to prevent the deep hydrogenation of cyclohexene to cyclohexane. It has been pointed out by Struijk et al. that the chemisorbed ZnSO<sub>4</sub> on the surfaces make the catalyst more hydrophilic and a more stable stagnant water layer is thus easily formed, resulting in a high yield of cyclohexene [7]. On the other hand, some ruthenium active sites may be occupied by ZnSO<sub>4</sub>, resulting in a decreased hydrogenation activity.



**Fig. 6.** Effect of ruthenium loading on the catalytic performance of CMZAR catalyst. Reaction conditions: H<sub>2</sub>/benzene = 2 (mol/mol), H<sub>2</sub>O/benzene = 1 (v/v), P = 3.0 MPa, T = 423 K, C(ZnSO<sub>4</sub>) = 0.5%, catalyst amount = 3.6 ml and LHSV = 4 h<sup>-1</sup>.



**Fig. 7.** Effect of the concentration of ZnSO<sub>4</sub> on the catalytic performance of 0.6% Ru/Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>/cordierite. Reaction conditions: H<sub>2</sub>/benzene = 2 (mol/mol), H<sub>2</sub>O/benzene = 1 (v/v), P = 3.0 MPa, T = 423 K, catalyst amount = 3.6 ml and LHSV = 4 h<sup>-1</sup>.

Notably, when the concentration of ZnSO<sub>4</sub> increases, the catalyst turns into to be much more hydrophilic and more active sites will be occupied by ZnSO<sub>4</sub>. A synergetic effect between the hydrophilicity and the apparent activity of the catalyst should be considered to achieve high cyclohexene yield. A more detailed investigation on the effect of the Zn/Ru is desired to be done in the future work.

### 3.6. Comparison of the monolithic catalyst with Asahi's catalyst

To obtain a high cyclohexene yield and make a comparison between the monolithic catalyst and Asahi's catalyst, a hydrogenation reaction was conducted on an optimized catalyst (0.6% Ru/Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>/cordierite) with a Zr/Al ratio of 0.116. As shown in Table 4, our catalyst gave a conversion of benzene of about 68–75% and the selectivity and yield of cyclohexene of 40–45% and 28–30%, respectively. Although our selectivity was lower than that of Asahi's catalyst, the cyclohexene yield was almost the same as Asahi's catalyst [4]. Additionally, production capacity of cyclohexene of our monolithic catalyst was a little higher than Asahi's catalyst, while the production of cyclohexane, which was not a desirable product but still an important raw material in chemical industry, was about four times more than Asahi's catalyst. Note that the separation apparatus for liquid and solid may not be necessary in the monolithic catalyst and the catalyst loss could be negligible. The amplification effect of the monolithic catalyst

**Table 4**  
Performance of monolithic catalyst and Asahi technology.

	Asahi	Monolithic catalyst <sup>a</sup>
Conversion (%)	35–40	68–75
Selectivity (%)	70–80	40–45
Yield (%)	28–30	28–30
Capacity (kg/kg Ru h)		
Cyclohexene	40–45	49–53
Cyclohexane	10–18	75–80
Separation of L-S	Yes	No
Catalyst loss	Severe	Negligible
Agitation	Necessary	No
Amplification effect	Severe	Minor

<sup>a</sup> Reaction conditions: P = 4.0 MPa, T = 423 K, LHSV = 0.75 h<sup>-1</sup>, C(ZnSO<sub>4</sub>) = 5% and H<sub>2</sub>/H<sub>2</sub>O/benzene = 1000:5:1 (v/v/v).

was also minor compared with Asahi's catalyst. Therefore, the monolithic catalyst/reactor overall shows some advantages in SHBC and the industrial application of the monolithic catalyst could be promising.

#### 4. Conclusions

Ru/Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>/cordierite showed satisfying catalytic performances than Ru/ZrO<sub>2</sub>/cordierite and Ru/Al<sub>2</sub>O<sub>3</sub>/cordierite, due to its high specific surface area and the large amount of large pores in Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>. Large pores in the coating layer benefits the internal mass-transfer of cyclohexene, inhibiting the consecutive hydrogenation of cyclohexene to cyclohexane. The optimized Zr/Al ratio was about 0.116 and an excess amount of zirconia in the Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> coating layer could negatively affect the specific surface area of Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> and the hydrogenation activity. An appropriate calcination temperature for Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> coating layer was found to be 1373 K. Concentration of ZnSO<sub>4</sub> needs to be increased with increasing ruthenium loading in order to keep Zn/Ru at a certain level to obtain high selectivity. Compared with the powder catalyst, monolithic catalysts showed some superior performances in the SHBC.

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