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Article

Ru/Al₂O₃-ZrO₂-NiO/cordierite monolithic catalysts for selective hydrogenation of benzene

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ABSTRACT

Ru/Al₂O₃-ZrO₂-NiO/cordierite catalysts with an egg-shell-like Ru distribution were prepared by conventional incipient wetness impregnation and ammonia gas absorption deposition. The performance of the catalysts in a modified monolithic fixed-bed reactor was evaluated. The catalysts exhibited good selectivity and stability. Importantly, a maximum yield of 24.7% was achieved at a low concentration of ZnSO₄ (0.5 wt%). The catalysts were characterized by N₂ adsorption, X-ray diffraction, inductively coupled plasma-atomic emission spectroscopy, optical microscopy, and scanning electron microscopy/energy-dispersive X-ray analysis. The introduction of NiO resulted in the formation of NiAl₂O₄ phase during calcination at 1373 K, reducing the proportion of small pores. Meanwhile, the presence of ZrO₂ enhanced the sintering resistance of the coating, and moderate surface area was retained after calcination. The egg-shell distribution of Ru, thin layer thickness indicating short diffusion length, small proportion of nanosized pores (e.g., 1–4 nm), moderate specific surface area, and narrow pore size distribution to facilitate Ru dispersion are thought to be important factors controlling the behavior of the present monolithic catalysts.

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1. Introduction

Cyclohexene is an attractive industrial intermediate for the synthesis of organic compounds [1] and a greener intermediate for the production of nylon and ε-caprolactam than KA oil produced by oxidation of cyclohexane [2]. The selective hydrogenation of benzene into cyclohexene was commercialized by Asahi Chemical Industry Co., Ltd. [3] and has attracted extensive academic and industrial interest in recent years. Sun et al. [4] developed nanocomposite Ru-Mn/ZrO₂ bimetallic catalysts containing nanoscale ZrO₂ as a dispersant, which gave a yield of cyclohexene of 61.3%.

We previously proposed an alternative to conventional four-phase slurry reactors [5], which is called the monolithic fixed-bed reactor (MFBR). The MFBR contains monolithic cata-

lysts with an egg-shell-like distribution and overcomes the inherent drawbacks of traditional slurry beds, such as the inevitable filtration step to separate microscale (less than 1 μm) catalyst, severe amplification effects, vigorous agitation, and catalyst attrition. Yields of 28%–30% were obtained using a Ru/Al₂O₃-ZrO₂ catalyst in the MFBR [5]. However, this catalyst rapidly deactivates so that the liquid hourly space velocity (LHSV) of benzene has to be decreased gradually to maintain the desired yield. The presence of zinc sulfate in high concentration (5%) [5,6] and the choking up of small pores [7] may be responsible for deactivation. Meanwhile, a reasonable yield could not be achieved at a low concentration of ZnSO₄ because of the numerous small pores in the Al₂O₃-ZrO₂ coating.

Hydrogenation of benzene into cyclohexene is thermodynamically much more unfavorable than hydrogenation into

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cyclohexane [8]. Therefore, introduction of additives that attach to the Ru surface to promote hydrophilicity and cyclohexene desorption [9] is needed in most of the cases [1–10]. Otherwise, the adsorbed cyclohexene would be rapidly hydrogenated into cyclohexane. It has been reported that inorganic modifiers such as Zn, Fe, Co, Ni, Cd, Ga, and In salts are more efficient than organic modifiers in this role [2]. However, corrosion of the reactor and deactivation of catalyst are more likely to occur in systems with a high concentration of inorganic additive. Struijk et al. [10] related decreasing reaction rate to poisoning of the catalysts by iron salts originating from the stainless steel reactor walls. Liu's results [9] obtained under pilot conditions indicated that the adsorption of Fe^{2+} sourced from the reaction vessel on the catalysts was the main reason for deactivation of the catalysts. Attempts have been made to prepare new catalysts to achieve high yields without any additive [6,11].

It has also been shown that pore structure plays an important role in promoting internal mass transfer and suppressing further hydrogenation of cyclohexene [5,12–16]. Ru does not disperse well on supports with wide pore distribution and large pore size, leading to a mixture of highly active sites with low selectivity and agglomerated Ru particles with low activity and selectivity [13,14]. Thus, we propose that a thin layer on the support, which has a moderate specific surface area, tailored pore structure, and fewer small pores, may help to improve the yield of cyclohexene at a low concentration of ZnSO_4 . To investigate this hypothesis, we introduced a series of metallic oxides, which can transform into spinel phase with Al_2O_3 via solid state reaction at high temperature ($> 800\text{ }^\circ\text{C}$), such as ZnO , MgO , and NiO , into the Al_2O_3 - ZrO_2 binary system and determined the effects of the coating structure. NiO was found to be the most effective promoter of those investigated. Therefore, we prepared a novel $\text{Ru}/\text{Al}_2\text{O}_3$ - ZrO_2 - NiO monolithic catalyst with an egg-shell-like structure with appropriate pore distribution and pore size by incipient wetness impregnation and ammonia gas absorption deposition (AD). Over this catalyst, comparable selectivity and yield for cyclohexene could be maintained using 0.5 wt% ZnSO_4 solution. The performance of the catalyst was evaluated in a MFBR. The $\text{Ru}/\text{Al}_2\text{O}_3$ - ZrO_2 - NiO catalyst was characterized by powder X-ray diffraction (XRD), N_2 adsorption measurements, optical microscopy, and scanning electron microscopy/energy-dispersive X-ray analysis (SEM-EDX). The stability of catalysts was also investigated.

2. Experimental

2.1. Catalyst preparation

Composites of metal oxides (Al_2O_3 - ZrO_2 - NiO) used as coating materials were prepared by the solution combustion method. Typically, appropriate amounts of nitrate precursors and urea were dissolved in deionized water (50 ml) and then decomposed at 773 K in a muffle oven. The resulting composites of metal oxides were wet-milled with a planetary mixer (BM-BP, Nanjing University Instrument Plant) for 12 h into an aqueous slurry for dip-coating.

Monolithic catalysts were prepared using the conventional dip-coating method. A block of 400 cpsi cordierite honeycomb (wall thickness = 0.18 mm) was cut into 9-cell cubic blocks with a length of 45 mm. The 9-cell blocks were immersed in the as-prepared slurry for 10 s and then withdrawn. The excess slurry in the channels was removed using compressed air with a flow rate of 1 m^3/h . The dipped blocks were rotated around their central axes for 1 min to achieve an even distribution and then dried in a microwave oven for 3 min. The coated blocks were then calcined in static air at 1373 K for 2 h. If not specified, the loading amount of each coating was adjusted to 7–8 wt% of the bare cordierite by varying the viscosity of the slurry using deionized water. The resultant coatings with different molar ratios are denoted AlZr_xNi_y , where x represents the molar ratio of Zr atoms to Al atoms, and y represents the molar ratio of Ni atoms to Al atoms.

As a typical incipient wetness impregnation process, the honeycomb blocks were impregnated with an aqueous solution of RuCl_3 (40 mg/ml) for 30 s. The excess solution was removed, and the blocks were dried under a flow of hot air. After calcination in air at 573 K for 2 h, $\text{Ru}/\text{Al}_2\text{O}_3$ - ZrO_2 - NiO monolithic catalysts with a Ru loading of 1.2 wt% were obtained. The monolithic catalysts are denoted $\text{Ru}/\text{AlZr}_x\text{Ni}_y$.

Ruthenium hydroxide is the precursor of active component in Asahi industrial catalysts [17]. To deposit ruthenium hydroxide onto the AlZr_xNi_y coating, a new method called ammonia gas AD was used. After the excess solution of RuCl_3 in the channels of the impregnated block was removed using compressed air with a flow rate of 1 m^3/h , NH_3 was flowed over the monolithic channels at a flow rate of 1 m^3/h for 3 min. The block was washed three times with deionized water and dried using hot air. The synthesized catalyst (denoted $\text{Ru}/\text{AlZr}_x\text{Ni}_y$ -AD) was then directly loaded into the reactor to be reduced by H_2 gas without calcination.

2.2. Catalyst characterization

The specific surface area of the AlZr_xNi_y coating on the channel wall was determined based on nitrogen adsorption measurements at 77 K with a Quantachrome Nova 2200e analyzer. The BET multipoint method was used to estimate the specific surface area. The pore distribution was calculated from the desorption isotherm using the BJH method. The structure of the coating was characterized by XRD (Rigaku D/max-A) with $\text{Cu K}\alpha$ radiation ($\lambda = 0.1541\text{ nm}$). Optical microscope observation was carried out using an Olympus microscope. SEM images and EDX linear scanning profiles were recorded with an FEI Quanta-2000 scanning electron microscope equipped with an EDX analyzer. The loading of AlZr_xNi_y coating on each block was determined by calculating the increase of weight after calcination at 1373 K. The Ru content in the $\text{Ru}/\text{AlZr}_x\text{Ni}_y$ catalyst was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES).

2.3. Catalyst performance test

Catalysts containing 1.2 wt% Ru and an AlZr_xNi_y coating

were tested for their propensity to hydrogenate benzene to cyclohexene in a modified testing unit similar to that reported elsewhere [5]. Instead of a 52-cell block with a dispenser, the 9-cell block with the attached catalyst was fixed directly below the ϕ 3-mm input tube without a dispenser. There was no space left between the block and input tube to ensure the reproducibility of gas-liquid distribution. The inner surface of the reactor tube contained a Teflon lining to prevent the reactant from directly contacting the stainless steel of the reactor tube, which may be the cause of deactivation in other systems because of metal ions released from the reaction vessel under the severe hydrothermal and corrosive conditions generally used. A detailed description of the operating procedure has been previously reported [5]. First, the monolithic catalyst loaded in the cylindrical reactor was reduced by high purity H_2 (purity > 99.9999%) at 473 K for 10 h and then pretreated with 0.5 wt% $ZnSO_4$ solution at 423 K for 2 h before reaction. Then H_2 gas (purity > 99.9999%), 0.5 wt% $ZnSO_4$ aqueous solution and benzene were introduced as reactants to start the reaction, which was performed at 473 K for 10 h. The product mixture was sampled at intervals and analyzed by a gas chromatograph equipped with a PEG-20M column and an FID detector.

3. Results and discussion

3.1. Effect of NiO introduction

To determine the preferential molar ratio of NiO (value of y), $Ru/AlZr_{0.115}Ni_y$ catalysts with different molar ratios of NiO were characterized. Table 1 presents the pore structure properties of the $Ru/AlZr_{0.115}Ni_y$ catalysts, while the catalytic performance of $Ru/AlZr_{0.115}Ni_y$ with different molar ratios of NiO is listed in Table 2. The BET surface area of the catalysts decreases as the ratio of Ni/Al increases, and the catalytic activity decreases accordingly. $Ru/AlZr_{0.115}Ni_{0.5}$ exhibited good performance with regard to both yield (8.5%) and selectivity (61.3%) because of its appropriate surface area and large proportion (55%) of the pore volume in the range of 7–18 nm. These results are consistent with our previous ones [5,12]. The $Ru/AlZr_{0.115}Ni_{0.1}$ catalyst was more active than $Ru/AlZr_{0.115}Ni_{0.5}$ but showed

poor selectivity (40.7%) despite $Ru/AlZr_{0.115}Ni_{0.1}$ having a larger average pore size than $Ru/AlZr_{0.115}Ni_{0.5}$. This is probably because the large pore volume of $Ru/AlZr_{0.115}Ni_{0.1}$ increases the internal diffusion resistance and residence time of the intermediate, making it more difficult for cyclohexene to diffuse into the external liquid phase. Meanwhile, the $Ru/AlZr_{0.115}Ni_1$ catalyst exhibited poor performance (yield 2.6%) even though it had a moderate BET surface area. The absence of pores in the range of 1–7 nm suggests that the Ru component is poorly dispersed inside coating after calcination at 573 K, resulting in blockage of the 1–7 nm pores in the impregnation process, which may be the main reason for the poor performance over the $Ru/AlZr_{0.115}Ni_1$ catalyst.

XRD patterns of the $AlZr_{0.115}Ni_y$ coatings with different molar ratios of NiO are depicted in Fig. 1(a). The main diffraction peaks at $2\theta = 31.41^\circ$, 37.01° , 45.0° , 59.66° , and 65.54° were identified as characteristic peaks of nickel aluminate spinel ($NiAl_2O_4$, JCPDS 10-0339). The peaks of the $AlZr_{0.115}Ni_{0.1}$ coating are shifted to the right side compared with those of the other samples. Similar spectra have been interpreted in the literature as indicative of $NiAl_2O_4$ spinel with a decreased cubic lattice parameter caused by the uptake of Al_2O_3 into the spinel structure [18]. This is also consistent with the spectra observed by Matsuzaki et al. [19]. In contrast, excess NiO in $AlZr_{0.115}Ni_1$ had no visible influence upon the textural properties of the coating. No obvious peaks from $\alpha-Al_2O_3$ (JCPDS 46-1212) and NiO (JCPDS 47-1049) were detected for the $AlZr_{0.115}Ni_{0.5}$ coating, confirming that Al_2O_3 and NiO transformed homogeneously

Table 1
Pore structure properties of the $Ru/AlZr_{0.115}Ni_y$ catalysts.

Catalyst	Pore size (nm)	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore volume ratio(%)	
				1–7 nm	7–18 nm
$Ru/AlZr_{0.115}Ni_{0.1}$	17.5	39.1	0.171	10	36
$Ru/AlZr_{0.115}Ni_{0.5}$	13.4	31.6	0.106	8.5	55
$Ru/AlZr_{0.115}Ni_1$	18.7	23.4	0.112	—	85

Table 2
Catalytic performance of the $Ru/AlZr_{0.115}Ni_y$ catalysts.

Catalyst	Conversion (%)	Selectivity (%)	Yield (%)
$Ru/AlZr_{0.115}Ni_{0.1}$	18.8	40.7	7.7
$Ru/AlZr_{0.115}Ni_{0.5}$	13.8	61.3	8.5
$Ru/AlZr_{0.115}Ni_1$	3.4	76.5	2.6

Reaction conditions: H_2 /benzene = 2 (mol/mol), H_2O /benzene = 1 (v/v), LHSV = 8 h^{-1} , p = 3.0 MPa, T = 423 K.

Fig. 1. XRD patterns of $AlZr_{0.115}Ni_y$ with different molar ratios of NiO (a) and $AlZr_xNi_{0.5}$ with different molar ratios of ZrO_2 (b).

and entirely into NiAl_2O_4 by solid state sintering during calcination at 1373 K. This also indicates that the content of small pores in the coating can be reduced by the formation of NiAl_2O_4 . Furthermore, it is found that ZrO_2 exists mainly in the tetragonal phase (t- ZrO_2). The peak around 28.2° is characteristic of monoclinic ZrO_2 (m- ZrO_2) as a minor phase. However, no m- ZrO_2 was identified in the $\text{Ru}/\text{AlZr}_{0.115}\text{Ni}_{0.5}$ coating. This implies that the presence of excess Al_2O_3 and NiO could inhibit the transformation of ZrO_2 from m- ZrO_2 into t- ZrO_2 .

3.2. Effect of ZrO_2 content

The pore structure properties of the $\text{AlZr}_x\text{Ni}_{0.5}$ coatings before impregnation are presented in Table 3. Even after calcination at 1373 K, a Zr/Al molar ratio of 0.173 leads to the highest BET surface area and the largest pore volume of pores with a size of 7–18 nm. Figure 2(a) displays the pore distributions of the $\text{AlZr}_x\text{Ni}_{0.5}$ coatings. All of the coatings have a low amount of small pores. $\text{AlZr}_{0.173}\text{Ni}_{0.5}$ contains mesopores with a narrow pore distribution ranging from 5 to 20 nm.

Figure 1(b) shows the XRD patterns of the $\text{AlZr}_x\text{Ni}_{0.5}$ coatings with varying molar ratios of ZrO_2 . Judging from the diffraction peak broadening, the crystallinity and crystallite size of NiAl_2O_4 spinel in the $\text{AlZr}_0\text{Ni}_{0.5}$ coating are both much higher than those in the others. This suggests that the introduction of ZrO_2 could inhibit the sintering and growth of NiAl_2O_4 spinel crystallites. However, the crystallinity and crystallite size of t- ZrO_2 increase as the molar ratio of ZrO_2 increases. The presence of $\alpha\text{-Al}_2\text{O}_3$ phase reveals that Al_2O_3 has not completely transformed into NiAl_2O_4 spinel in the presence of excess ZrO_2 . It can be seen that excess ZrO_2 could not further enhance the resistance against sintering when the molar ratio of ZrO_2 exceeds 0.173, and only had a negative effect on BET surface area (Table 3).

Figure 2(b) illustrates the catalytic performance of $\text{Ru}/\text{AlZr}_x\text{Ni}_{0.5}$ with different molar ratios of ZrO_2 . The conversion of benzene at an LHSV of 4 h^{-1} increased from 16.2% to 35.3% when the Zr/Al molar ratio increased from 0 to 0.173, and then decreased to 11.3% when the Zr/Al molar ratio increased to 0.46. The Zr/Al molar ratio of 0.173 is the optimal value, resulting in maximum conversion (35.3%) and yield (17.7%). Notably, the trend of benzene conversion is in good accordance with the change of BET surface area, as shown in Table 3. Liu et al. [20] reported that high surface area of the support helps to improve dispersion of Ru after impregnation. High dispersion of Ru could improve the catalytic activity of the said selective hydrogenation reaction [23]. The Ru/

Fig. 2. Pore distribution of $\text{AlZr}_x\text{Ni}_{0.5}$ with different ratios of ZrO_2 (a) and their catalytic performance of $\text{Ru}/\text{AlZr}_x\text{Ni}_{0.5}$ (b). 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, LHSV = 4 h^{-1} .

$\text{AlZr}_{0.115}\text{Ni}_{0.5}$ catalyst demonstrated higher conversion than the $\text{Ru}/\text{AlZr}_{0.23}\text{Ni}_{0.5}$ catalyst probably because of the good dispersion of Ru related to the higher BET surface area of the coating. In addition, it has been reported that narrow pore distribution of the support (Fig. 2(a)) could facilitate the dispersion and stability of Ru by hindering the movement of Ru particles during the reaction [13]. Moreover, it seems plausible that large pores ranging from 7 to 18 nm in size improve the diffusion of cyclohexene, resulting in good selectivity [12]. Overall, the $\text{Ru}/\text{AlZr}_{0.173}\text{Ni}_{0.5}$ catalyst exhibited the highest yield.

3.3. Optical microscopy and SEM-EDX characterization

Figure 3(a) displays optical microscope images of cross-sections of the 9-cell block of the $\text{AlZr}_{0.173}\text{Ni}_{0.5}$ catalyst and a magnified cross-sectional view of the channel wall in the direction of the channel before and after Ru impregnation. Obvious boundaries are observed between the coating and bulk

Table 3

Pore structure properties of $\text{AlZr}_x\text{Ni}_{0.5}$ coatings on blocks calcined at 1373 K.

Coating	Pore size ^a (nm)	Surface area ^a (m^2/g)	Pore volume ^b (cm^3/g)	Pore volume ratio ^b		Pore volume ^b (cm^3/g)	
				1–7 nm	7–18 nm	1–7 nm	7–18 nm
$\text{AlZr}_0\text{Ni}_{0.5}$	20.6	16.0	0.083	11%	26%	0.0091	0.0022
$\text{AlZr}_{0.115}\text{Ni}_{0.5}$	11.6	30.2	0.094	28%	66%	0.026	0.058
$\text{AlZr}_{0.173}\text{Ni}_{0.5}$	13.5	42.3	0.149	17%	68%	0.025	0.125
$\text{AlZr}_{0.23}\text{Ni}_{0.5}$	12.0	22.2	0.068	20%	60%	0.014	0.041
$\text{AlZr}_{0.46}\text{Ni}_{0.5}$	12.5	9.8	0.035	38%	29%	0.013	0.010

^a Calculated based on the multipoint BET method. ^b Calculated using the BJH model.

Fig. 3. Optical microscope images showing the cross-section of the 9-cell block of the as-prepared Ru/AlZr_{0.173}Ni_{0.5} catalyst (a) and magnified cross-sectional views of the channel wall in the direction of the channel before (b) and after (c) Ru impregnation. SEM image (d) and EDX element profiles (e) of the as-prepared AlZr_{0.173}Ni_{0.5} catalyst.

cordierite. A fairly uniform, continuous layer formed on the bulk cordierite. The average thickness of this layer was calculated to be 10.7 μm by averaging the thicknesses measured from the magnified cross-sectional view of each channel. Comparing Fig. 3(b) and (c) clearly reveals that Ru is distributed within the AlZr_{0.173}Ni_{0.5} coating and hardly appears in the bulk cordierite.

The distribution of Ru over the cross-section of the catalyst

was examined by SEM-EDX with a linear scan. Figure 3(d) and (e) shows an SEM image of the cross-section of a typical channel wall and the element distribution profiles monitored by EDX analysis from bulk cordierite to the as-prepared AlZr_{0.173}Ni_{0.5} catalyst surface, respectively. The thickness of the AlZr_{0.173}Ni_{0.5} catalyst layer is 10.59 μm, which is in good agreement with the average thickness of this layer calculated above from optical microscope images. The observed results reveal the egg-shell distribution of Ru within the monolithic block. Similar results were obtained for the other studied catalysts with different molar ratios.

Figure 4 shows SEM images of the surface morphology of Ru/AlZr_xNi_{0.5} catalysts reduced by pure H₂ gas at 473 K for 10 h. Numerous micron-size slits and pores can be observed on the surface of the catalyst layer with a thickness of about 10 μm for all three catalysts. Formation of the coating layer can be divided into two steps in the present slurry coating process [24]: (1) the micron-size oxide particles suspended in the slurry agglomerate as the water is vaporized by the flow of hot air over the substrate surface; (2) during calcination, sintering reaction occurred at the points where the particles touch each other, causing the particles to connect to form a layer. Therefore, the micron-size pores in the layer correspond to the stacking intervals of the micron-size oxide particles. It is thought that the slits form by cracking of the layer during sintering at high temperature.

Although the Ru/AlZr_{0.173}Ni_{0.5} catalyst layer is thicker than that of a previously reported 0.6 wt% Ru/Al₂O₃-ZrO₂ catalyst (~7 μm) [12], the current catalyst layer showed superior selectivity and improved yield at an LHSV of 4 h⁻¹ with a 0.5wt% ZnSO₄ solution. This is because of the following reasons. (1) The micron-size slits and pores act as water reservoirs, resulting in a stagnant water layer formed by capillary force. It is believed that a stagnant water layer is essential to expel the

Fig. 4. SEM images showing the top view of surface morphology of Ru/AlZr_xNi_{0.5} catalyst layers reduced by pure H₂ gas at 473 K for 10 h. (a, b) Ru/AlZr_{0.115}Ni_{0.5}; (c, d) Ru/AlZr_{0.173}Ni_{0.5}; (e, f) Ru/AlZr_{0.23}Ni_{0.5}.

Fig. 5. Schematic diagram of the hydrogenation process over monolithic catalyst.

newly formed cyclohexene from the Ru surface because of the extremely low solubility of cyclohexene in water [6,19]. Thus, the water layer suppresses the consecutive hydrogenation of cyclohexene. (2) It is known that pore diffusion decreases the selectivity for cyclohexene [10,15,21–23]. The addition of NiO reduced the proportion of small pores because of the formation of NiAl_2O_4 spinel by solid state reaction and consequently increases the selectivity for cyclohexene. (3) The presence of ZrO_2 enhanced the resistance to sintering and grain growth of NiAl_2O_4 spinel. Adequate surface area was retained after calcination at 1373 K, which facilitated Ru dispersion. As a result, the $\text{Ru}/\text{AlZr}_{0.173}\text{Ni}_{0.5}$ catalyst exhibited good activity. (4) We tentatively suggest that the catalyst layer with micron-size slits and pores provides superior accessibility to active sites so that the desorbed cyclohexene can easily diffuse through the large slits and pores towards bulk organic phase, resulting in good selectivity. These points are summarized in Fig. 5.

3.4. Comparison of maximum yields

To evaluate the potential of the catalysts for industrial use, $\text{Ru}/\text{AlZr}_x\text{Ni}_{0.5}$ catalysts with different molar ratios of ZrO_2 ($x = 0.115, 0.173$, and 0.23) were tested while decreasing LHSV at set intervals to determine the maximum yield. The results obtained are shown in Table 4. The $\text{Ru}/\text{AlZr}_{0.173}\text{Ni}_{0.5}$ catalyst exhibited the highest activity. Nevertheless, a maximum yield of 24.7% could be obtained over the $\text{Ru}/\text{AlZr}_{0.115}\text{Ni}_{0.5}$ catalyst at lower LHSV (1.5 h^{-1}) than $\text{Ru}/\text{AlZr}_{0.173}\text{Ni}_{0.5}$. This result could be explained from two aspects. (1) The mass transfer limitation that slows the rate of cyclohexene readsorption helps to obtain a higher yield of cyclohexene, as described by Milone et al. [23]. (2) At a high conversion of benzene, it is believed that the only route left for cyclohexene escape is diffusion because the low

Table 4

Catalytic performance of $\text{Ru}/\text{AlZr}_x\text{Ni}_{0.5}$ at low LHSV.

Catalyst	LHSV (h^{-1})	Conversion (%)	Selectivity (%)	Yield (%)
$\text{Ru}/\text{AlZr}_{0.115}\text{Ni}_{0.5}$	1.5	60.7	40.7	24.7
$\text{Ru}/\text{AlZr}_{0.173}\text{Ni}_{0.5}$	2.0	61.9	36.2	22.3
$\text{Ru}/\text{AlZr}_{0.23}\text{Ni}_{0.5}$	2.0	51.3	39.4	20.2

Reaction conditions: $\text{H}_2/\text{benzene} = 2$ (mol/mol), $\text{H}_2\text{O}/\text{benzene} = 1$ (v/v), $p = 3.0 \text{ MPa}$, $T = 423 \text{ K}$.

concentration gradient of benzene is not enough to form cyclohexene droplets in the water layer [10]. Based on a calculation method we proposed previously [25], the Carberry number (Ca) and the Wheeler-Weisz number ($\eta\phi^2$) for cyclohexene were estimated to be 0.186 and 0.050, respectively, while these values were 0.148 and 0.045, respectively, for the $\text{Ru}/\text{AlZr}_{0.115}\text{Ni}_{0.5}$ catalyst. Both of these values are much higher than the previous results obtained over $\text{Ru}/\text{Al}_2\text{O}_3$ ($\text{Ca} = 0.048$ and $\eta\phi^2 = 0.015$) [25]. As a consequence, it can be imagined that the production of cyclohexene is controlled by the external diffusion limitation of cyclohexene at a high conversion of benzene. Consecutive hydrogenation of the cyclohexene produced by selective hydrogenation would be more likely to occur inside the catalyst layer because of the high porosity of the $\text{AlZr}_{0.173}\text{Ni}_{0.5}$ coating as the cyclohexene concentration gradient decreases. In consequence, appropriate porosity of the coating layer, including both macro- and microporosity, is an important factor to realize an acceptable yield.

Besides structural factors, the acidity of the support has been reported as an important factor in tailoring catalyst behavior. Zhou et al. [26] reported that minimizing the amount of Lewis acid sites increases selectivity for cyclohexene. It is thought that calcination at 1373 K could lead to complete depletion of acid sites. This might also improve the selectivity for cyclohexene.

3.5. Comparison of stability

To make the results comparable with a previous report, 0.6% $\text{Ru}/\text{Al}_2\text{O}_3\text{-ZrO}_2$ and 0.6% $\text{Ru}/\text{AlZr}_{0.173}\text{Ni}_{0.5}$ catalysts were prepared by incipient wetness impregnation and ammonia gas AD, respectively, and tested for their stability at high conversion of benzene (>60%) for a period of about 30–35 h. Figure 6 illustrates stability profiles showing the space-time conversion of benzene ($\text{kg}/(\text{L}_{\text{cat}}\cdot\text{h})$) and space-time yield of cyclohexene ($\text{kg}/(\text{L}_{\text{cat}}\cdot\text{h})$) over the catalysts. Although the $\text{Ru}/\text{Al}_2\text{O}_3\text{-ZrO}_2$ catalyst exhibited the best performance initially, its activity gradually halved over 30 h. In contrast, the activity and yield obtained for both $\text{Ru}/\text{AlZr}_{0.173}\text{Ni}_{0.5}$ and $\text{Ru}/\text{AlZr}_{0.173}\text{Ni}_{0.5}\text{-AD}$ catalysts remained almost stable over about 35 h. This is probably because the $\text{AlZr}_{0.173}\text{Ni}_{0.5}$ coating contains few small pores that are easily choked up during reaction and reversible deactivation because adsorption of Zn^{2+} onto the active sites became much slower at a low concentration of Zn^{2+} . It is interesting to note that the activity and stability of $\text{Ru}/\text{AlZr}_{0.173}\text{Ni}_{0.5}\text{-AD}$ catalyst are even higher than those of the $\text{Ru}/\text{AlZr}_{0.173}\text{Ni}_{0.5}$ catalyst. Further research into the reason for this is in progress.

Fig. 6. Stability of space-time conversion (a) and space-time yield (b) over different monolithic catalysts. Reaction conditions: H_2 /benzene = 2 (mol/mol), H_2O /benzene = 1 (v/v), $p = 3.0$ MPa, $T = 423$ K, $C(ZnSO_4)$ for $Ru/AlZr_{0.173}Ni_{0.5} = 0.5$ wt%, $C(ZnSO_4)$ for $Ru/AlZr_{0.173}Ni_{0.5}-AD = 1$ wt%, $C(ZnSO_4)$ for $Ru/Al_2O_3-ZrO_2(0.115) = 5$ wt%.

4. Conclusions

$Ru/Al_2O_3-ZrO_2-NiO$ /cordierite catalysts with an egg-shell-like Ru distribution and thin coating layer (ca. 10 μm thick) were prepared by conventional incipient wetness impregna-

tion and ammonia gas absorption deposition. Their catalytic performance was evaluated in a modified monolithic fixed-bed reactor. Compared with a previously reported $Ru/Al_2O_3-ZrO_2$ catalyst, the $Ru/Al_2O_3-ZrO_2-NiO$ catalyst showed comparable selectivity, higher stability, and a maximum yield of 24.7% at a low concentration of $ZnSO_4$ (0.5 wt%). The egg-shell distribution of Ru, thin layer thickness indicating short diffusion length, fewer small pores (e.g., 1–4 nm), moderate specific surface area, and narrow pore size distribution to facilitate Ru dispersion may all be crucial to the catalytic activity and selectivity of this monolithic catalyst. Nevertheless, at high conversion of benzene, the production of cyclohexene is controlled by the diffusion limitation of cyclohexene. Accordingly, a compromise between catalytic performance and porosity should be taken into account to obtain a high yield of cyclohexene for industrial applications.

References

- [1] Hronec M, Cvengrosová Z, Kralík M, Palma G, Corain B. *J Mol Catal A*, 1996, 105: 25
- [2] Liu J L, Zhu Y, Liu J, Pei Y, Li Z H, Li H, Li H X, Qiao M H, Fan K N. *J Catal*, 2009, 268: 100
- [3] Nagahara H, Ono M, Konishi M, Fukuoka Y. *Appl Surf Sci*, 1997, 121/122: 448
- [4] Sun H J, Jiang H B, Li S H, Wang H X, Pan Y J, Dong Y Y, Liu S C, Liu Z Y. *Chin J Catal* (孙海杰, 江厚兵, 李帅辉, 王红霞, 潘雅洁, 董英英, 刘寿长, 刘仲毅. 催化学报), 2013, 34: 684
- [5] Zhao Y J, Zhou J, Zhang J G, Wang S D. *Catal Commun*, 2008, 9: 459
- [6] Mizukami F, Niwa S, Ohkawa S, Katayama A. *Stud Surf Sci Catal*, 1993, 78: 337
- [7] Hao Y X, Li J S, Yang X J, Wang X, Lu L D. *Mater Sci Eng A*, 2004, 367: 243
- [8] Hu S C, Chen Y W. *Ind Eng Chem Res*, 2001, 40: 6099
- [9] Liu S C, Liu Z Y, Wang Z, Wu Y M, Yuan P. *Chem Eng J*, 2008, 139: 157
- [10] Struijk J, d'Angremond M, Lucas de Regt W J M, Scholten J J F. *Appl*

Graphical Abstract

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$Ru/Al_2O_3-ZrO_2-NiO$ /cordierite monolithic catalysts for selective hydrogenation of benzene

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Novel egg-shell-like $Ru/Al_2O_3-ZrO_2-NiO$ /cordierite monolithic catalysts with tailored pore structure are fabricated. Mesopores and low pore volume are needed to obtain a reasonable yield of cyclohexene using the monolithic catalysts with a low concentration of $ZnSO_4$ solution.

- Catal A*, 1992, 83: 263
- [11] Fan G Y, Jiang W D, Wang J B, Li R X, Chen H, Li X J. *Catal Commun*, 2008, 10: 98
- [12] Zhao Y J, Zhou J, Zhang J G, Wang S D. *J Mol Catal A*, 2009, 309: 35
- [13] Fukuzawa A. WO Patent 2006/006277. 2006
- [14] Furuya M, Fukuoka Y, Fukuzawa A. JP Patent 2002154990A. 2002
- [15] Struijk J, Moene R, van der Kamp T, Scholten J J F. *Appl Catal A*, 1992, 89: 77
- [16] Liu Z Y, Sun H J, Wang D B, Guo W, Zhou X L, Liu S C, Li Z J. *Chin J Catal* (刘仲毅, 孙海杰, 王栋斌, 郭伟, 周小莉, 刘寿长, 李中军. 催化学报), 2010, 31: 150
- [17] Nagahara H, Konishi M. US Patent 4 734 536. 1988
- [18] Han Y S, Li J B, Ning X S, Yang X Z, Chi B. *Mater Sci Eng A*, 2004, 369: 241
- [19] Matsuzaki T, Fukuda Y, Yamasaki O. *Stud Surf Sci Catal*, 2007, 172: 571
- [20] Liu S C, Luo G, Han M L, Li Z G. *Chin J Catal* (刘寿长, 罗鸽, 韩民乐, 李中军. 催化学报), 2001, 22: 559
- [21] Struijk J, Scholten J J F. *Appl Catal A*, 1992, 82: 277
- [22] Hu S C, Chen Y W. *Ind Eng Chem Res*, 2001, 40: 3127
- [23] Milone C, Neri G, Donato A, Musolino M G, Mercadante L. *J Catal*, 1996, 159: 253
- [24] Nijhuis T A, Beers A E W, Vergunst T, Hoek I, Kapteijn F, Moulijn J A. *Catal Rev-Sci Eng*, 2001, 43: 345
- [25] Zhao Y J, Zhou J, Zhang J G, Li D Y, Wang S D. *Ind Eng Chem Res*, 2008, 47: 4641
- [26] Zhou G B, Liu J L, Tan X H, Pei Y, Qiao M H, Fan K N. *Ind Eng Chem Res*, 2012, 51: 12205

用于苯选择加氢的Ru/Al₂O₃-ZrO₂-NiO/堇青石蜂窝整体催化剂

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摘要: 使用浸涂法和氨气吸收沉积法制备了新型用于苯选择加氢的具有蛋壳型分布的Ru/Al₂O₃-ZrO₂-NiO/堇青石蜂窝整体催化剂,且在固定床整体反应器中对其性能进行了测试. 该催化剂显示了较优的选择性和稳定性,并且在低的ZnSO₄浓度(0.5%问题)下环己烯产物收率可达24.7%. 采用N₂吸附-脱附法,电感耦合等离子体发射光谱,光学显微镜,扫描电子显微镜及能量色散X射线光谱仪等技术研究了影响催化剂性能的因素. 结果表明,NiO的引入减少了涂层中的微孔含量,有利于在低的添加剂浓度下提高环己烯选择性. ZrO₂的存在抑制了涂层的烧结,保证涂层在1373 K高温焙烧后仍有较大的比表面积. Ru的蛋壳分布、薄的涂层厚度、较少的微孔含量、较大的比表面积和狭窄的孔分布可能是影响整体蜂窝催化剂中该特殊催化行为的重要因素.

关键词: 整体催化剂; 涂层; 苯; 环己烯; 选择性加氢; 尖晶石; 氧化锆; 氧化镍

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