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Communication

Selective hydrogenation of benzene to cyclohexene in continuous reaction device with two reaction reactors in serie over Ru-Co-B/ZrO₂ catalysts

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ARTICLE INFO

Article history:

Received 18 April 2013

Accepted 20 June 2013

Published 20 August 2013

Keywords:

Benzene

Selective hydrogenation

Cyclohexene

Ruthenium

Transition metal

Boron

ABSTRACT

A Ru-B/ZrO₂ catalyst for selective hydrogenation of benzene to cyclohexene was prepared using a chemical reduction method. The effects of transition metals such as Cr, Mn, Fe, Co, Ni, Cu, and Zn on the performance of the Ru-B/ZrO₂ catalyst were investigated. It was found that the addition of these transition metals all increased the B content of the Ru-B/ZrO₂ catalyst. The modification of B, the ensemble effect, and the ligand effect of the second metal or metal oxide resulted in a decrease in the activity and an increase in the selectivity for cyclohexene of the Ru-B/ZrO₂ catalyst. When the atomic ratio of Co/Ru was 0.06, the Ru-Co-B/ZrO₂ catalyst gave a selectivity for cyclohexene of 82.8% and a cyclohexene yield of 62.8% at a benzene conversion of 75.8% at 25 min. Moreover, the benzene conversion was stable at around 40%, and the selectivity for cyclohexene and the cyclohexene yields stabilized at around 73% and 30%, respectively, in 419 h under the optimum reaction conditions in a continuous device with two reactors in series.

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The production of nylon-6 and nylon-66 from benzene via cyclohexene has the advantages of safety, atomic economy, and being environmentally friendly, compared with the use of benzene and cyclohexane [1,2]. Supported amorphous alloy Ru catalysts have attracted much attention because they not only exhibit high activities and high selectivities for cyclohexene but also have the merits of better utilization of the Ru noble metal and ease of use in industry [3–6].

In our preliminary work, with the help of the enterprises, our group investigated the activity, cyclohexene selectivity, modifiable character, regeneration, and life-time of a

Ru-La-B/ZrO₂ catalyst in a series device with a 100 L stainless-steel autoclave [7,8]. In this device, the Ru-La-B/ZrO₂ catalyst gave a better performance than the Ru-Zn catalyst obtained from the Asahi Chemical Company. However, the benzene conversion and the selectivity for cyclohexene were only 20% and 55%, respectively, because of device defects. In this work, the effects of transition metals as promoters on the performance of the Ru-B/ZrO₂ catalyst were systematically investigated. The Ru-Co-B/ZrO₂ catalyst with the optimum Co/Ru molar ratio of 0.06 gave high activity and the best cyclohexene yield. Moreover, the performance of the Ru-Co-B/ZrO₂ catalyst for selective

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This work was supported by the National Natural Science Foundation of China (21273205), the Innovation Found for Technology Based Firms of China (10C26214104505), the China Postdoctoral Science Foundation (2012M511125), and the Scientific Research Foundation of Graduate School of Zhengzhou University.

DOI: 10.1016/S1872-2067(12)60637-8 | <http://www.sciencedirect.com/science/journal/18722067> | Chin. J. Catal., Vol. 34, No. 8, August 2013

hydrogenation of benzene to cyclohexene was tested for the first time in a continuous device with two reactors in series.

The catalysts were prepared according to the procedure reported in the literature [9]. The preparation procedure for the Ru-Co-B/ZrO₂ catalyst is given as an example. ZrO₂ (7.0 g) was added to 200 mL of a solution containing 2.90 g of RuCl₃·3H₂O and a desired amount of CoCl₂·6H₂O, with stirring; agitation was continued for 30 min. To this suspension, 100 mL of NaBH₄ solution (0.8 mol/L) were quickly added dropwise under stirring at room temperature; stirring was continued for 5 min. The black precipitate was filtered and washed thoroughly with distilled water until neutrality, giving the desired Ru-Co-B/ZrO₂ catalyst. The catalyst was divided into two portions; one portion was used for activity tests and the other was used for catalyst characterization. This method ensured that catalysts promoted with the different transition metals had the same Ru contents (about 0.5 g). The amount of CoCl₂·6H₂O was adjusted to give catalysts with different nominal Co/Ru molar ratios; these catalysts were denoted by Ru-Co(*x*)-B/ZrO₂, where *x* is the nominal Co/Ru molar ratio. The Ru-M-B/ZrO₂ catalysts were prepared in a manner similar to that used to prepare the Ru-Co-B/ZrO₂ catalysts, excepted that CoCl₂·6H₂O was replaced by equal molar amounts of Cr(NO₃)₃·9H₂O, MnSO₄·H₂O, FeSO₄·7H₂O, NiSO₄·7H₂O, CuSO₄·5H₂O, or ZnSO₄·7H₂O. Ru-M(*x*)-B/ZrO₂ denotes the Ru-B/ZrO₂ catalysts promoted with different transition metals, where *x* represents the nominal M/Ru molar ratio.

The compositions of the catalysts were analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) using an ICAT 6000 Series instrument (Heme Electron Corporation).

The selective hydrogenation of benzene was performed in a 1 L Hastelloy-lined autoclave. A sample of Ru-M(*x*)-B/ZrO₂ catalyst, 49.2 g of ZnSO₄·7H₂O, and 280 mL of water were charged in the autoclave. Heating was begun under a H₂ pressure of 5 MPa and a stirring rate of 800 r/min. Benzene (140 mL) was fed into the system and the stirring rate was increased to 1400 r/min to exclude diffusion effects. The reaction process was monitored by taking small samples of the reaction mixture every 5 min. The products were analyzed using gas chromatography (GC; Hangzhou Kexiao Instruments Co., GC-1690).

The performance of Ru-Co(0.06)-B/ZrO₂ was tested in a continuous device with two reactors in series according to the following procedure. A schematic diagram of the device is shown in Fig. 1. Each reactor has a capacity of 300 L and is made of Hastelloy. Ru-Co(0.06)-B/ZrO₂ catalyst (5 kg), 500 L of water, and 88 kg of ZnSO₄·7H₂O were added to reactors 1 and 2 from the catalyst feed inlet 5 and the catalyst holding tank 6. The autoclave was purged four times with N₂ to remove air that entered through the N₂ inlet 2. Then the N₂ was flushed out four times using H₂ through the H₂ inlet 1. The slurry circulation pump 10 was started with a slurry cycling speed of 647 L/h under a H₂ pressure of 5 MPa and a stirring rate of 300 r/min. The benzene feed pump 4 was started with a benzene feeding speed of 150 L/h when the temperature reached 140 °C. After separation of the organic phase and the slurry in the settling tank, the slurry was pumped into reactor 1 by the slur-

Fig. 1. Schematic diagram of the continuous reaction device with two reaction reactors in series. 1—H₂ inlet; 2—N₂ inlet; 3—benzene feed inlet; 4—benzene feed pump; 5—catalyst feed inlet; 6—catalyst holding tank; 7—reactor 1; 8—reactor 2; 9—settling tank; 10—slurry circulation pump; 11—slurry flow meter; 12—product outlet; —□—control valve; SL—low-pressure steam; WCR—returning cooling water; TIC—temperature indication controller; WC—cooling water; CCL—low-pressure circumfluent condensate; LDIC—level difference indication controller; SC—solenoid-controlled valve.

ry cycling pump 10. The temperature was controlled at 140 ± 5 °C. The organic phase was sampled hourly, followed by GC analysis.

Table 1 shows the benzene conversions and selectivities for cyclohexene at the maximum yield in 25 min over the Ru-M(*x*)-B/ZrO₂ catalysts. As can be seen, the Ru-B/ZrO₂ catalyst gave a selectivity for cyclohexene of 72.8% and a cyclohexene yield of 61.1% at a benzene conversion of 83.9% in the 1 L Hastelloy-lined autoclave. This indicates that the Ru-B/ZrO₂ catalyst inherently exhibited a high activity and excellent selectivity for cyclohexene in the absence of any promoter. The activities of the Ru-M(*x*)-B/ZrO₂ catalysts all decreased, and the selectivities for cyclohexene all increased, with increasing

Table 1

Benzene conversions and selectivities for cyclohexene at maximum yield at 25 min over Ru-M(*x*)-B/ZrO₂ catalysts.

Catalyst	Conversion (%)	Selectivity (%)	Yield (%)
Ru-B/ZrO ₂	83.9	72.8	61.1
Ru-Cr(0.06)-B/ZrO ₂	44.0	82.4	36.3
Ru-Cr(0.21)-B/ZrO ₂	24.1	84.3	20.3
Ru-Mn(0.06)-B/ZrO ₂	69.6	78.5	54.6
Ru-Mn(0.21)-B/ZrO ₂	64.3	80.0	51.4
Ru-Fe(0.06)-B/ZrO ₂	53.5	80.9	43.3
Ru-Fe(0.21)-B/ZrO ₂	28.6	89.9	25.7
Ru-Co(0.06)-B/ZrO ₂	75.8	82.8	62.8
Ru-Co(0.21)-B/ZrO ₂	68.8	81.4	56.0
Ru-Ni(0.06)-B/ZrO ₂	50.4	81.7	41.1
Ru-Ni(0.21)-B/ZrO ₂	31.5	85.9	27.1
Ru-Cu(0.06)-B/ZrO ₂	50.9	85.3	43.4
Ru-Cu(0.21)-B/ZrO ₂	22.9	90.1	20.6
Ru-Zn(0.06)-B/ZrO ₂	76.4	76.8	58.6
Ru-Zn(0.21)-B/ZrO ₂	60.4	82.4	49.7

Reaction conditions: in the 1 L Hastelloy-lined autoclave, a share of catalyst with the Ru content of about 0.5 g, 45.7 g ZnSO₄·7H₂O, 280 mL H₂O, 5 MPa H₂, 150 °C, stirring rate of 1400 r/min.

amount of the second transition metal added. Obviously, the increase in cyclohexene selectivity is at the expense of catalytic activity, which is consistent with reports in the literature [1,10]. When the nominal Co/Ru molar ratio was 0.06, the activity of the Ru-Co-B/ZrO₂ catalyst decreased slightly, but the selectivity for cyclohexene significantly increased. Moreover, the best cyclohexene yield, i.e., 62.8%, was obtained over this catalyst. The addition of Cr, Mn, Fe, Co, Ni, Cu, or Zn resulted in increased selectivity for cyclohexene, but the activities of the catalysts decreased significantly. The cyclohexene yields obtained using the catalysts with these transition metals as promoters were lower than that obtained using Ru-B/ZrO₂.

Table 2 shows the compositions of the Ru-M-B/ZrO₂ catalysts determined using ICP-AES. As can be seen, increasing the amounts of transition metals used as promoters increased the B contents of the catalysts, indicating that the added transition metals could adjust the B contents in the catalysts. It is known that the B content is an important factor in catalysts for selective hydrogenation of benzene to cyclohexene [9,11,12]. The B species in the Ru catalysts are mainly present in two forms: the elemental state and the oxidative state. The role of B species can be understood based on the following considerations. (1) The oxidative B species on the catalyst surface could bond with water molecules through hydrogen bonds. This significantly enhances the hydrophilicity of the catalyst, which could accelerate desorption and hinder re-adsorption of cyclohexene for hydrogenation to cyclohexane. The selectivity for cyclohexene is therefore improved [9,12]. (2) The elemental B species could donate electrons to the Ru species, making the B species electron deficient and the Ru species electron rich. The electron-deficient B species could easily accept the lone pair on the oxygen in water [12], promoting water adsorption on the catalyst surface. This increases the hydrophilicity of the catalyst and improves the selectivity for cyclohexene. In addition, the electron-rich Ru species are also beneficial for the desorption of cyclohexene. The adsorption of water on the catalyst surface and the electron-rich Ru species could also prevent adsorption of benzene, resulting in decreased catalytic activity.

The ensemble effect and the ligand effect of the transition metals or metal oxides also have significant effects on the per-

formances of the catalysts in selective hydrogenation of benzene to cyclohexene. The ensemble effect means that the presence of transition metals or metal oxides could cause a geometric arrangement of the Ru active sites and might reduce or dilute Ru active sites for the hydrogenation of cyclohexene to cyclohexane, resulting in increased selectivity for cyclohexene [10]. The ligand effect means that the presence of transition metals or metal oxides could enhance the catalyst hydrophilicity, leading to a decrease in the adsorption enthalpies for H₂, benzene, or cyclohexene. The selectivities of the catalysts for cyclohexene therefore increase [10]. Struijk et al. [13] proposed that chemisorbed Zn²⁺ could not only increase the catalyst hydrophilicity but could also selectively cover the most reactive sites. This decreased the adsorption enthalpies of benzene and cyclohexene, increasing the desorption rate and the selectivity for cyclohexene. Fan et al. [4] prepared a Ru-Co-B/γ-Al₂O₃ catalyst and found that the Co promoter improved the selectivity for cyclohexene. They found that the Co species existed in the catalyst as oxides, and suggested that the presence of Co oxides could create a micro-environment that was unfavorable for further hydrogenation of cyclohexene to cyclohexane. Specifically, the Co oxides could occupy the active sites, on which cyclohexene is quickly hydrogenated to cyclohexane. The selectivity for cyclohexene therefore increases. Also, there is electron transfer from Ru species to the Co oxides [4]. The adsorbability of cyclohexene on the electron-deficient Ru is weak, and it is easy for cyclohexene to be desorbed from the catalyst surface, and so the selectivity for cyclohexene increases [4,14]. The addition of a second metal or metal oxide therefore improves the selectivity of the Ru-B/ZrO₂ catalyst.

Obviously, Co is the best promoter for the Ru-B/ZrO₂ catalyst; it significantly increased the selectivity for cyclohexene and the cyclohexene yield, and slightly decreased the activity. The Ru-Co(0.06)-B/ZrO₂ catalyst gave the best cyclohexene yield as a result of the synergistic effects among the active component Ru, the Co promoter, and the B species.

The effect of the stirring rate on the performance of the Ru-Co(0.06)-B/ZrO₂ catalyst was investigated at a benzene feeding rate of 200 L/h and a slurry cycling rate of 647 L/h. The results are summarized in Fig. 2(a). Increasing the stirring rate increased the selectivity for cyclohexene and the cyclohexene yield, but decreased the activity. When the stirring rate was 450 r/min, the benzene conversion was stable at around 45%, and the selectivity for cyclohexene and the cyclohexene yield stayed at around 73% and 33%, respectively. This indicates that mass transport limitation at the gas/liquid interface and the liquid/liquid interface is minimized at a stirring rate of 450 r/min. However, further increasing the stirring rate to 500 r/min decreased the benzene conversion and the cyclohexene yield. This suggests that the higher stirring rate prevented the mass transport of benzene or H₂, resulting in a decrease in the reaction rate. Struijk et al. [15] also observed the same phenomenon. They thought that the catalysts easily suffered from attrition and adhesion to the inner wall of the reactor.

The effect of the benzene feeding rate on the performance of the Ru-Co(0.06)-B/ZrO₂ catalyst was investigated at a stirring rate of 450 r/min and a slurry cycling rate of 647 L/h. The re-

Table 2
Compositions of Ru-M-B/ZrO₂ catalysts measured by ICP-AES.

Catalyst	B content (wt%)	M content (wt%)
Ru-B/ZrO ₂	0.065	0
Ru-Cr(0.06)-B/ZrO ₂	0.277	0.282
Ru-Cr(0.21)-B/ZrO ₂	0.331	0.655
Ru-Mn(0.06)-B/ZrO ₂	0.144	0.441
Ru-Mn(0.21)-B/ZrO ₂	0.205	0.985
Ru-Fe(0.06)-B/ZrO ₂	0.118	0.108
Ru-Fe(0.21)-B/ZrO ₂	0.221	1.196
Ru-Co(0.06)-B/ZrO ₂	0.152	0.124
Ru-Co(0.21)-B/ZrO ₂	0.181	0.761
Ru-Ni(0.06)-B/ZrO ₂	0.129	0.186
Ru-Ni(0.21)-B/ZrO ₂	0.207	0.734
Ru-Cu(0.06)-B/ZrO ₂	0.078	0.266
Ru-Cu(0.21)-B/ZrO ₂	0.100	1.337
Ru-Zn(0.06)-B/ZrO ₂	0.078	0.437
Ru-Zn(0.21)-B/ZrO ₂	0.321	1.813

Fig. 2. Performance of Ru-Co(0.06)-B/ZrO₂ catalyst for selective hydrogenation of benzene to cyclohexene in a continuous reaction device with two reactors in series. (a) Effect of stirring rate; (b) Effect of benzene feeding rate; (c) Effect of slurry cycling rate; (d) Catalyst stability under optimum conditions. Reaction conditions: catalyst 5 kg, water 500 L, ZnSO₄·7H₂O 88 kg, 140 ± 5 °C, 4.5 ± 0.5 MPa H₂.

sults are shown in Fig. 2(b). When the benzene feeding rate was increased from 150 to 230 L/h, the benzene conversion slightly decreased, but the selectivity for cyclohexene and the cyclohexene yield gradually increased. Increasing the benzene feeding rate could promote the desorption of cyclohexene dissolved in benzene and increase the selectivity for cyclohexene. When the benzene feeding rate was decreased from 230 to 200 L/h, although the selectivity for cyclohexene decreased slightly, the benzene conversion and the cyclohexene yield increased significantly. This indicates that the optimum benzene feeding rate was 200 L/h, at which the catalyst provided a higher cyclohexene yield and a higher reaction rate.

The effect of the slurry cycling rate on the performance of the Ru-Co(0.06)-B/ZrO₂ catalyst was investigated at a stirring rate of 450 r/min and a benzene feeding rate of 200 L/h. The results are shown in Fig. 2(c). When the slurry cycling rate was decreased from 647 to 504 L/h, the benzene conversion, the selectivity for cyclohexene, and the cyclohexene yield all decreased. This indicates that increasing the slurry cycling rate favors mass transport of the reactants, i.e., benzene and H₂, improving the reaction rate. Moreover, increasing the slurry cycling rate is also beneficial for the desorption of cyclohexene, so the selectivity for cyclohexene increased. However, the slurry cycling rate could not be increased further because of limitations imposed by the volume of the settling tank.

The stability and lifetime of Ru-Co(0.06)-B/ZrO₂ were in-

vestigated at a stirring rate of 450 r/min, a benzene feeding rate of 200 L/h, and a slurry cycling rate of 647 L/h. The results are shown in Fig. 2(d). The benzene conversion stabilized at around 40%, and the selectivity for cyclohexene and the cyclohexene yield remained at around 73% and 30%, respectively, up to 419 h; this is close to the cyclohexene yield of 32% achieved with an industrial Ru-Zn catalyst. However, it should be noted that the Ru content of Ru-Co(0.06)-B/ZrO₂ was only one-quarter that of the industrial Ru-Zn catalyst. This indicates that the Ru-Co(0.06)-B/ZrO₂ catalyst not only has excellent selectivity for cyclohexene and good stability but also has better noble metal utilization. The mass ratio of benzene/Ru was 0.26 in the 1 L autoclave, but it was only 0.12 in the continuous device. The performance of Ru-Co(0.06)-B/ZrO₂ in the continuous device did not reach the same level as that in the 1 L autoclave because of the limitations of the continuous device (such as defects in the settling tank). The benzene conversion and cyclohexene yields decreased significantly. The Zn and Fe contents in the catalyst were 2.17% and 0.57%, respectively, determined using ICP-AES, indicating that the chemisorption of large amounts of Zn²⁺ and Fe²⁺ led to deactivation of the catalyst. It was found that large areas of the walls of reactors 1 and 2 were corroded, as shown in Fig. 3, and this was the main source of Fe²⁺. However, the activity and the selectivity of the catalyst for cyclohexene were recovered by washing out the chemisorbed Zn²⁺ and Fe²⁺ with HCl solution [8].

Graphical Abstract

Chin. J. Catal., 2013, 34: 1482–1488 doi: 10.1016/S1872-2067(12)60637-8

Selective hydrogenation of benzene to cyclohexene in continuous reaction device with two reaction reactors in serie over Ru-Co-B/ZrO₂ catalysts

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The selectivity for cyclohexene and the cyclohexene yield were stabilized at around 73% and 30%, respectively, in 419 h over a Ru-Co-B/ZrO₂ catalyst in a continuous device with two reactors in series.

Fig. 3. Deeply corroded reactor.

In summary, the Ru-Co(0.06)-B/ZrO₂ catalyst exhibited excellent selectivity for cyclohexene and good stability, indicating its good prospects for industrial applications. It was found that the activity and the selectivity of the catalyst for cyclohexene in a continuous device with two reactors in series were higher than those achieved using a single reactor [7,8]. One of the biggest advantages of the continuous device with two reactors in series is enlargement of the reactor volume, which enables the slurry cycling rate and the benzene feeding rate to be increased. This results in good contact between benzene and the catalyst, and improved desorption of cyclohexene, increasing the catalytic activity and selectivity for cyclohexene.

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串联双釜连续反应装置中Ru-Co-B/ZrO₂上苯选择加氢制环己烯

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摘要: 采用化学还原法制备了苯选择加氢制环己烯催化剂Ru-B/ZrO₂, 考察了Cr, Mn, Fe, Co, Ni, Cu和Zn等过渡金属的添加对

Ru-B/ZrO₂催化剂性能的影响。结果表明, 这些过渡金属的添加均可提高Ru-B/ZrO₂催化剂中的B含量。B的修饰及第二种金属或金属氧化物的集团效应和配位效应导致Ru-B/ZrO₂催化剂活性降低和环己烯选择性升高。当Co/Ru原子比为0.06时, Ru-Co-B/ZrO₂催化剂上反应25 min苯转化率为75.8%时, 环己烯选择性和收率分别为82.8%和62.8%。在双釜串联连续反应器和优化反应条件下, Ru-Co-B/ZrO₂催化剂使用419 h内苯转化率稳定在40%左右, 环己烯选择性和收率分别稳定在73%和30%左右。

关键词: 苯; 选择加氢; 环己烯; 钌; 过渡金属; 硼

收稿日期: 2013-04-18. 接受日期: 2013-06-20. 出版日期: 2013-08-20.

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基金来源: 国家自然科学基金(21273205); 国家科技型中小企业创新基金(10C26214104505); 中国博士后科学基金(2012M511125); 郑州大学优秀博士论文培育基金。

本文的英文电子版由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).

由苯出发经环己烯制备尼龙6和尼龙66比经环己烷路线具有安全、碳原子经济和环境友好等特点^[1,2]。化学还原法制备的负载型非晶态合金Ru基催化剂不但在苯选择加氢反应中表现出高活性和高环己烯选择性, 而且具有贵金属利用率高和易工业化等优点, 引起了人们的极大关注^[3-6]。

本课题组曾与企业联合, 在100 L不锈钢单釜连续反应装置上考察了Ru-La-B/ZrO₂催化剂的活性、环己烯选择性、可调变性、再生和寿命等重要指标^[7,8], 发现该催化剂性能明显优于进口Ru-Zn催化剂。然而由于反应装置的原因, 苯转化率仅为20%, 环己烯选择性仅为55%。本文系统考察了过渡金属对Ru-B/ZrO₂催化剂性能的影响, 并在串联双釜连续反应器中考察了Ru-Co-B/ZrO₂催化剂的苯选择加氢制环己烯性能。

参照文献[9]制备催化剂。在搅拌下将2.90 g RuCl₃·3H₂O和一定量的CoCl₂·6H₂O溶于200 mL水中, 加入7.0 g ZrO₂, 继续搅拌30 min; 于室温快速滴入100 mL NaBH₄溶液(0.8 mol/L)。滴加完毕后, 继续搅拌5 min。然后抽滤至洗涤液为中性, 即得Ru-Co-B/ZrO₂催化剂。平均分为2份, 分别用于催化剂评价和表征, 确保用于加氢的各催化剂中Ru含量相同(0.5 g)。调整CoCl₂·6H₂O用量, 制得不同Co/Ru原子比的Ru-Co(x)-B/ZrO₂, 其中x为Co/Ru理论原子比。以同样方法制得Ru-M(x)-B/ZrO₂催化剂(M = Cr, Mn, Fe, Co, Ni, Cu或Zn), 各金属M的前驱体分别为Cr(NO₃)₃·9H₂O, MnSO₄·H₂O, FeSO₄·7H₂O, NiSO₄·7H₂O, CuSO₄·5H₂O和ZnSO₄·7H₂O。

催化剂组成在Heme Electron公司的ICAT 6000 SERIES型电感耦合等离子原子发射光谱仪(ICP-AES)上测定。

Ru-M(x)-B/ZrO₂催化剂评价在1 L GS-1型哈氏合金釜中进行。加入一份Ru-M-B/ZrO₂催化剂, 49.2 g ZnSO₄·7H₂O和280 mL H₂O。在5 MPa H₂压力和800 r/min转速下升温至150 °C后加入140 mL苯, 调节转速至

1400 r/min, 每隔5 min取样, 在GC-1690型气相色谱仪(杭州科晓)上分析产物组成。

串联双釜连续反应器(见图1)中Ru-Co(0.06)-B/ZrO₂催化剂评价按如下步骤进行。每个反应釜的体积为300 L, 釜材质为哈氏合金。从催化剂进口5和催化剂储藏罐6将5 kg Ru-Co(0.06)-B/ZrO₂催化剂、500 L水和88 kg ZnSO₄·7H₂O加入到反应器1和2中。通过氮气进气口2, 用氮气置换釜内空气4次, 再经氢气进气口1, 用氢气置换釜内氮气4次。调节H₂压至5 MPa, 转速300 r/min。开启浆液循环泵10, 调节浆液循环速率为647 L/h。升温至140 °C后, 开启苯进料泵4, 苯进料流量为150 L/h。有机相与浆液在沉降槽(770 L)分离后, 浆液经浆液循环泵10打入反应釜1。控制反应温度在140 ± 5 °C。每隔1 h取样。在GC-1690型气相色谱仪上分析产物组成。

表1给出了Ru-M-B/ZrO₂催化剂上反应25 min内最高环己烯收率时苯转化率和环己烯选择性。可以看出, 在1 L哈氏合金釜中Ru-B/ZrO₂上苯转化率为83.9%时环己烯选择性和收率分别为72.8%和61.1%, 说明不加任何助剂的Ru-B/ZrO₂催化剂具有较高的活性和环己烯选择性。随着过渡金属的加入及其量的增加, 催化剂活性降低, 环己烯选择性升高。可见, 环己烯选择性的升高是以牺牲活性为代价的, 与文献[1,10]一致。当Co/Ru原子比为0.06时, Ru-Co-B/ZrO₂催化剂的活性略有下降, 环己烯选择性则显著升高, 其收率达62.8%; 而第二助剂Cr, Mn, Fe, Co, Ni, Cu和Zn的加入则使环己烯选择性升高的同时, 反应活性显著降低, 环己烯收率也更低。

表2为Ru-M-B/ZrO₂催化剂的组成。可以看出, 随着第二种助剂含量的增加, 催化剂中B含量增加, 说明所加过渡金属可以调节催化剂中的B含量, 而B含量是影响苯选择加氢制环己烯催化剂性能的重要因素^[9,11,12]。Ru催化剂中B主要以游离态和氧化态两种形式存在。氧化态的B可以通过氢键与水分子键合, 提高催化剂的亲水性, 加速生成环己烯的脱附, 抑制脱附环己烯的再吸附

并加氢生成环己烷, 环己烯选择性增加^[9,12]. 游离态的B可以将部分电子转移给Ru, 使得B缺电子, Ru富电子. 缺电子的B更容易接受水中O的孤对电子, 促进了H₂O在催化剂表面的吸附, 因而催化剂亲水性增强, 环己烯选择性升高. 富电子的Ru有利于生成的环己烯脱附. 另外, 水的吸附和Ru的富电子又抑制了苯在催化剂表面上的吸附, 从而导致催化剂活性降低^[12].

第二种助剂金属或金属氧化物的集团效应和配位效应也是影响苯选择加氢制环己烯催化剂性能的另一个重要因素. 集团效应是指第二助剂金属或金属氧化物的存在导致活性组分金属Ru的几何重排, 减少或稀释了环己烯加氢的Ru活性位, 从而提高环己烯选择性^[10]. 配位效应为第二助剂金属或金属氧化物的存在增加了Ru催化剂亲水性, 使得H₂、苯或环己烯化学吸附焓降低, 因而环己烯选择性升高^[10]. Struijk等^[13]认为, 化学吸附的Zn²⁺不但可以增加催化剂亲水性, 而且可以选择覆盖一部分最强的活性位, 从而降低苯和环己烯在催化剂表面的吸附焓, 提高环己烯的脱附速率, 增大环己烯选择性. Fan等^[4]制备了Ru-Co-B/ γ -Al₂O₃催化剂, 发现Co可提高环己烯选择性. 他们发现催化剂中Co以氧化物存在, 从而创造了一个不利于环己烯继续加氢的微环境. 首先氧化钴可以占据环己烯很快加氢的活性位, 因而环己烯选择性升高; 其次, Ru可以将部分电子转移给氧化钴^[4], 缺电子的Ru上环己烯吸附能力差, 易脱附, 因而环己烯选择性升高^[4,14]. 总之, 第二助剂金属或金属氧化物的加入提高了环己烯选择性.

综上所述, Co的加入显著提高了Ru-B/ZrO₂催化剂上环己烯选择性和收率(62.8%), 其活性略有下降, 促进效果最佳.

在苯进料速率和浆液循环速率分别为200和647 L/h的条件下, 考察了搅拌速率对Ru-Co(0.06)-B/ZrO₂催化剂性能的影响, 结果见图2(a). 可以看出, 随着搅拌速率的增加, 苯转化率逐渐降低, 环己烯选择性和收率逐渐升高; 至450 r/min时苯转化率稳定在45%左右, 环己烯选择性和收率分别稳定在73%和33%左右, 表明在450 r/min时气-液和液-液之间界面的传质阻力最小. 继续增加搅拌速率至500 r/min, 苯转化率和环己烯收率降低, 表明较快的搅拌抑制了气-液和液-液界面的传质, 使得反应速率下降, 与文献[15]一致. 在较高的搅拌下催化

剂易破损, 且易粘附在反应器壁上.

在搅拌速率和浆液循环速率分别为450 r/min和647 L/h的条件下, 考察了苯进料速率对Ru-Co(0.06)-B/ZrO₂催化剂性能的影响, 结果见图2(b). 可以看出, 当苯进料速率从150 L/h升至230 L/h, 苯转化率略有下降, 但环己烯选择性和收率逐渐提高. 苯进料速率的提高有利于溶解在苯中的环己烯溢出, 因此选择性增加. 当苯进料速率又降低至200 L/h, 虽然环己烯选择性略有降低, 但苯转化率和环己烯收率显著提高. 可见, 苯进料速率控制在200 L/h为宜.

在搅拌速率和苯进料速率分别为450 r/min和200 L/h的条件下, 考察了浆液循环速率对Ru-Co(0.06)-B/ZrO₂催化剂性能的影响, 结果见图2(c). 当浆液循环量由647 L/h降至504 L/h时, 苯转化率、环己烯选择性和收率均降低, 表明较高的浆液循环速率不但有利于反应物苯和H₂的传质, 提高了反应速率, 而且有利于环己烯的溢出, 提高环己烯选择性. 然而浆液循环量受制于沉降槽的体积.

图2(d)给出了Ru-Co(0.06)-B/ZrO₂催化剂的稳定性和寿命. 可以看出, 反应419 h以前, 苯转化率稳定在40%左右, 环己烯选择性和收率分别稳定在73%和30%左右, 后者与目前工业催化剂的接近(32%). 但本催化剂中Ru用量仅为工业Ru-Zn催化剂的1/4. 可见, Ru-Co(0.06)-B/ZrO₂催化剂不但具有较高的环己烯选择性和稳定性, 而且贵金属利用率高. 需要特别指出的是, 小试中苯/Ru质量比为0.26, 而串联双釜中苯/Ru质量比仅为0.12, 同时由于反应釜条件的限制(如沉降槽的设计缺陷等), Ru-Co(0.06)-B/ZrO₂催化剂性能并未达到单釜(1 L)水平. 另外, 反应419 h以后苯转化率和环己烯收率急剧降低. ICP测得Ru-Co(0.06)-B/ZrO₂中Zn和Fe含量分别为2.17%和0.57%, 说明大量化学吸附的Zn²⁺和Fe²⁺导致了催化剂的失活. 打开反应釜, 发现反应器壁大面积腐蚀, 如图3所示, 这是Fe²⁺的主要来源. 然而, 用HCl洗去化学吸附的Fe²⁺和Zn²⁺可恢复催化剂活性和选择性^[6].

总之, 在串联双釜连续反应装置中, 反应容积明显增加, 因而Ru-Co(0.06)-B/ZrO₂催化剂在苯选择加氢反应中表现出较高的活性和选择性, 明显优于单釜连续反应装置^[7,8], 且具有良好的稳定性, 具有较大的工业应用潜力.