二乙醇胺作添加剂 Ru-Zn 催化剂上苯选择加氢制环己烯

孙海杰, 潘雅洁, 王红霞, 董英英, 刘仲毅*, 刘寿长

郑州大学化学系, 河南郑州450001

摘要: 采用共沉淀法制备了 Ru-Zn 催化剂, 考察了二乙醇胺的添加对 Ru-Zn 催化剂上苯选择加氢制环己烯性能的影响, 并采用 N₂ 物理吸附、透射电镜、X 射线衍射、X 射线荧光、傅里叶变换红外和程序升温还原等手段对催化剂进行了表征。结果表明, 二乙醇胺可以与浆液中 ZnSO₄ 反应生成 (Zn(OH)₂)₃(ZnSO₄)(H₂O)₃ 和硫酸二乙醇胺盐。随着二乙醇胺用量的增加, 化学吸附在催化剂表面的 (Zn(OH)₂)₃(ZnSO₄)(H₂O)₃ 增多, 它与硫酸二乙醇胺盐的协同作用提高了 Ru-Zn(4.9%) 催化剂上苯选择加氢生成环己烯的选择性。当二乙醇胺用量为 0.3 g 时, (Zn(OH)₂)₃(ZnSO₄)(H₂O)₃ 在 Ru-Zn(4.9%) 催化剂加氢后样品的表面高度分散, 反应性能最佳, 循环使用第 3 次时苯转化率为 84.3%, 环己烯选择性和收率分别达 75.5% 和 63.6%; 使用至第 4 次时, 反应 25 min 时苯转化率和环己烯选择性仍可达 75% 以上, 环己烯收率为 58% 以上。

关键词: 二乙醇胺; 钌; 锌; 苯; 选择加氢; 环己烯

中图分类号: O643

文献标识码: A

收稿日期: 2011-10-21. 接受日期: 2011-11-21.

*通讯联系人. 电话: (0371)67783384; 电子信箱: liuzhongyi@zzu.edu.cn

基金来源: 国家科技型中小企业创新基金 (02C26214100384, 10C26214104505).

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

Selective Hydrogenation of Benzene to Cyclohexene over a Ru-Zn Catalyst with Diethanolamine as an Additive

SUN Haijie, PAN Yajie, WANG Hongxia, DONG Yingying, LIU Zhongyi*, LIU Shouchang

Department of Chemistry, Zhengzhou University, Zhengzhou 450001, Henan, China

Abstract: A Ru-Zn catalyst was prepared by co-precipitation, and the effect of adding diethanolamine on benzene selective hydrogenation to cyclohexene was investigated. The catalyst was characterized by N₂ physisorption, transmission electron microscopy, X-ray diffraction, X-ray fluorescence, Fourier transform infrared spectroscopy, and temperature-programmed reduction. Diethanolamine reacted with ZnSO₄ in the slurry to form (Zn(OH)₂)₃(ZnSO₄)(H₂O)₃ and diethanolamine sulfate. The amount of (Zn(OH)₂)₃(ZnSO₄)(H₂O)₃ adsorbed on the catalyst surface increased with the increase in the diethanolamine amount. The synergism of (Zn(OH)₂)₃(ZnSO₄)(H₂O)₃ and diethanolamine sulfate improved the cyclohexene selectivity of the Ru-Zn(4.9%) catalyst. With a diethanolamine dosage of 0.3 g, (Zn(OH)₂)₃(ZnSO₄)(H₂O)₃ was highly dispersed on catalyst surface and the sample after hydrogenation was characterized. This catalyst exhibited the best performance with a cyclohexene selectivity and yield of 75.5% and 63.6%, respectively, at the benzene conversion of 84.3% in the third run. Moreover, the benzene conversion and cyclohexene selectivity were stable above 75% and cyclohexene yield was above 58% in the fourth run.

Key words: diethanolamine; ruthenium; zinc; benzene; selective hydrogenation; cyclohexene

Received 21 October 2011. Accepted 21 November 2011.

*Corresponding author: Tel: +86-371-67783384; E-mail: liuzhongyi@zzu.edu.cn

This work was supported by the Innovation Found for Technology Based Firms of China (02C26214100384, 10C26214104505).

English edition available online at Elsevier ScienceDirect (<http://www.sciencedirect.com/science/journal/18722067>).

由苯经环己烯制尼龙-6 和尼龙-66 比经环己烷的路线具有经济、安全、节能和环境友好等特点, 一

直为人们所关注^[1~3]。然而, 苯选择加氢生成环己烯的 ΔG 为 -23 kJ/mol , 而苯完全加氢生成环己烷的为

-98 kJ/mol^[1], 表明苯加氢制环己烯是非常困难的。因此, 高选择性苯加氢制环己烯催化体系的研发是该技术的核心。

助剂和添加剂对催化剂表面的亲水性修饰是提高 Ru 基催化剂上苯选择加氢生成环己烯选择性的主要方法。1989 年, 日本旭化成公司利用无负载 Ru-Zn 催化剂和纳米 ZrO₂ 分散剂率先实现了苯选择加氢制环己烯的工业化, 当苯转化率为 40% 时, 环己烯选择性和收率分别为 80% 和 32%^[4,5]。Liu 等^[6]利用双溶剂浸渍法制备了 Ru-Ce/SBA-15 催化剂, Ce/Ru 摩尔比为 0.25 时在溶液 (0.42 mol/L ZnSO₄) 中进行苯加氢反应的环己烯收率为 53.8%。进而他们又以 ZnSO₄ 和 CdSO₄ 为双添加剂, 使得 Ru-La/SBA-15 催化剂上苯转化率为 82% 时, 环己烯选择性和收率分别为 69% 和 57%^[7]。Liu 等^[8]制备了 Ru-Cu/ZnO 催化剂, 当 Ru/Cu 摩尔比为 10 时, 在 2 ml 的 NaOH 溶液 (0.3 mol/L) 中反应, 苯转化率和环己烯选择性分别为 72.3% 和 68.3%。虽然环己烯收率都明显高于工业催化剂的, 但环己烯选择性不到 70%, 不能满足工业要求^[9]。

本课题组制备了单层分散型 Ru-Zn 催化剂, 在苯加氢反应 20 min 时苯转化率 84.8%, 环己烯选择性为 69.8%^[2]。我们还制备了双助剂 Ru-Mn-Zn 催化剂, 在 Mn/Zn 摩尔比为 0.3 和添加 0.5 g 的 NaOH 时, 反应 5 min 苯转化率为 60.2% 时, 环己烯选择性高达 81.1%; 至 20 min 时环己烯收率最高达到 59.9%^[10]。我们还简要报道了在 Ru-Zn 催化剂上用 PEG-20000 和二乙醇胺作添加剂时环己烯收率分别为 61.4% 和 58.9%^[3]。本文考察在反应修饰剂硫酸锌存在下二乙醇胺量对 Ru-Zn 催化剂性能的影响, 并对使用后催化剂进行表征, 探讨二乙醇胺对 Ru-Zn 催化剂的作用机理。

1 实验部分

1.1 催化剂的制备

参照文献 [11] 制备催化剂。将一定量 RuCl₃·3H₂O 和 ZnSO₄·7H₂O 溶于 200 ml 蒸馏水中, 搅拌下快速加入 30% NaOH 溶液 200 ml, 于 80 °C 搅拌 4 h。静置后弃去上层清液, 所得黑色固体用 5% NaOH 溶液洗涤 3 次, 分散于 5% NaOH 溶液中后移至高压釜中还原。在 H₂ 压 5.0 MPa 和 800

r/min 搅拌下升温至 150 °C, 还原 3 h 后取出, 用 5% NaOH 洗涤 3 次, 再用蒸馏水洗涤至中性, 即得 Ru-Zn 催化剂。不同 Zn 含量的催化剂记作 Ru-Zn(x), 其中 x 为原子吸收光谱测得的催化剂中 Zn 的含量。

1.2 催化剂的表征

催化剂中 Zn 含量在 Perkin Elmer AAnalyst 300 型原子吸收光谱仪上测定。λ = 213.9 nm, 狭缝宽度为 0.20 nm。样品织构性质在 Quantachrome 公司 Nova 1000e 型物理吸附仪上测定。样品的形貌在 JEOL JEM 2100 型透射电子显微镜 (TEM) 上观察。样品的物相分析在 PANalytical 公司 X'Pert PRO 型 X 射线衍射 (XRD) 仪上进行。Cu K_α 射线, 管电压 40 kV, 管电流 40 mA, 扫描范围 2θ = 5°~90°, 扫描步长 0.03°。样品中各元素含量分析在 Bruker 公司 S4 Pioneer 型 X 射线荧光仪 (XRF) 上进行。傅里叶变换红外光谱 (FT-IR) 在 Thermo Nicolet 公司 Nexus-470 型红外光谱仪测得, 采用 KBr 压片法制样。程序升温还原 (TPR) 在自组装微型反应装置上进行。以 5% H₂-95% N₂ (流量 30 ml/min) 为还原气, 升温速率为 10 °C/min, TCD 检测耗氢量。

1.3 催化剂的评价

苯选择加氢反应在 GS-1 型哈氏合金釜中进行。加入 1.96 g Ru-Zn 催化剂, 9.8 g ZrO₂, 49.2 g ZnSO₄·7H₂O, 280 ml H₂O 和一定量的二乙醇胺。在 H₂ 压力为 5.0 MPa 和搅拌速率为 800 r/min 的条件下, 升温至 150 °C 后加入 140 ml 苯, 调节转速至 1400 r/min (以消除外扩散), 每隔 5 min 取样。采用杭州科晓 GC-1690 型气相色谱仪分析产物组成, FID 检测器, 面积校正归一法计算产物浓度, 进而计算苯转化率和环己烯选择性。反应完成后, 用分液漏斗分离除去有机相, 催化剂和 ZrO₂ 连同反应浆液再次加入到高压反应釜中, 不补加任何物质, 其它条件同上进行反应。反应后固体样品洗涤后留作表征。初次使用后和循环使用后的固体样品分别记作 Ru-Zn(x)-y 和 Ru-Zn(x)-R。其中, y 为二乙醇胺的质量 (g), R 为循环。

2 结果与讨论

2.1 催化剂的表征结果

2.1.1 样品的织构性质

ZrO₂, Ru-Zn 催化剂及二乙醇胺作添加剂

Ru-Zn 催化剂加氢后样品的结构性质列于表 1. 可以看出, Ru-Zn(4.9%) 的比表面积、孔径和孔体积分别为 $62 \text{ m}^2/\text{g}$, 5.74 nm 和 $0.089 \text{ cm}^3/\text{g}$. 经加氢和循环使用后, 催化剂的比表面积、孔径和孔体积与 ZrO_2 的接近. 这与 ZrO_2 用量 (ZrO_2 与催化剂的质量比为 5) 有关.

表 1 ZrO_2 和 Ru-Zn 催化剂及不同量二乙醇胺作添加剂 Ru-Zn 催化剂加氢后样品的结构性质

Table 1 Textural properties of ZrO_2 , Ru-Zn catalyst and the Ru-Zn(4.9%) catalyst with different diethanolamine dosages as an additive after hydrogenation

Sample	$A/(\text{m}^2/\text{g})$	d/nm	$V/(\text{cm}^3/\text{g})$
ZrO_2	34	15.99	0.130
Ru-Zn(4.9%)	62	5.74	0.089
Ru-Zn(4.9%)-0	37	19.88	0.179
Ru-Zn(4.9%)-0.2	35	10.58	0.092
Ru-Zn(4.9%)-0.3	36	17.78	0.159
Ru-Zn(4.9%)-0.4	37	13.26	0.124
Ru-Zn(4.9%)-R	42	15.74	0.168

The x in Ru-Zn(x) catalyst represents the Zn content determined by atomic absorption spectroscopy; Ru-Zn(x)- y is the Ru-Zn(x) catalyst sample after hydrogenation and y is the diethanolamine dosage; Ru-Zn(4.9%)-R is Ru-Zn(4.9%) catalyst sample after 5 recycles.

2.1.2 TEM 结果

图 1 为各 Ru-Zn(4.9%) 催化剂的 TEM 照片及其微晶尺寸分布. 可以看出, Ru-Zn(4.9%) 催化剂颗粒的微晶尺寸集中在 3.5 nm ; 加入 0.3 g 二乙醇胺作添加剂经初次反应后催化剂颗粒被 ZrO_2 分隔开了. 这说明适量的 ZrO_2 可以抑制在反应过程中因催化剂颗粒与颗粒之间碰撞而聚结, 且可减小催化剂颗粒粘附在反应器器壁上的几率^[12]. 同时适量的 ZrO_2 可以增加环己烯选择性^[13]. 还可以看出, 使用一次后催化剂的微晶尺寸集中分布在 3.5 nm , 与新鲜催化剂的近似; 经循环使用 5 次后, 仅增至 3.8 nm . 而 Ru-Zn 催化剂中主要成分纳米 Ru 金属颗粒很难分散且易于聚结长大. 由此可见, 加入 ZrO_2 可起到很好的分散作用.

2.1.3 XRD 结果

图 2 为 Ru-Zn(4.9%) 催化剂及不同二乙醇胺添加量的 Ru-Zn 催化剂加氢后的 XRD 谱. 可以看出, Ru-Zn(4.9%) 催化剂在 $2\theta = 38.4^\circ, 42.4^\circ, 43.9^\circ, 58.3^\circ, 69.3^\circ$ 和 78.3° 出现了 Ru 特征峰 (JCPDS

图 1 各 Ru-Zn 样品的 TEM 照片及其微晶尺寸分布

Fig. 1. TEM images and the crystallite size distribution of different catalyst samples.

图 2 Ru-Zn(4.9%) 催化剂及不同量二乙醇胺作添加剂 Ru-Zn 催化剂加氢后样品的 XRD 谱

Fig. 2. XRD patterns of the Ru-Zn(4.9%) catalyst and the catalyst samples with different diethanolamine dosages as an additive after the hydrogenation.

01-070-0274). 孙海杰等^[2]的研究已表明, Ru-Zn 催化剂中大部分 Zn 以 ZnO 存在;但也有报道认为催化剂中 Zn 以金属态存在^[14~16]. 由于样品中未出现 ZnO 或 Zn 的衍射峰,说明 Zn 物种高度分散或其微晶尺寸小于检出限. 当二乙醇胺用量为 0~0.3 g 时,使用后的 Ru-Zn(4.9%) 催化剂样品在 $2\theta = 43.9^\circ$ 处出现微弱 Ru 的特征峰 (JCPDS 01-070-0274),其余均为单斜相 ZrO_2 的特征峰 (JCPDS 00-024-1165). 当二乙醇胺用量为 0.4 g 时,相应催化剂还在 $2\theta = 9.8^\circ$ 处出现了 $(\text{Zn}(\text{OH})_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_3$ 的特征峰 (JCPDS 01-078-0247). 这表明二乙醇胺和浆液中 ZnSO_4 反应生成了 $(\text{Zn}(\text{OH})_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_3$, 如反应式 (1) 和式 (2) 所示.

当二乙醇胺用量为 0.3 g 时, $(\text{Zn}(\text{OH})_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_3$ 高度分散于 Ru-Zn(4.9%) 催化剂和分散剂 ZrO_2 表面. 循环使用 5 次后, Ru-Zn(4.9%) 催化剂中 Ru 的衍射峰明显减弱,说明在循环使用过程中催化剂在与油相分离时有所流失. 二乙醇胺用量为 0.3 g, Ru-Zn(8.4%) 催化剂加氢后样品也出现了 $(\text{Zn}(\text{OH})_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_3$ 特征峰. 本课题组研究发现, Ru-Zn(8.4%) 中的 Zn 一部分以 ZnO 的形式

存在, 催化剂表面的 ZnO 可与浆液中 ZnSO_4 反应生成 $\text{ZnSO}_4 \cdot 3\text{Zn}(\text{OH})_2 \cdot 7\text{H}_2\text{O}$ (JCPDS 00-009-0204), 并分散在催化剂表面上. 加入的二乙醇胺同样能与浆液中的 ZnSO_4 反应生成 $(\text{Zn}(\text{OH})_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_3$, 后者与 $\text{ZnSO}_4 \cdot 3\text{Zn}(\text{OH})_2 \cdot 7\text{H}_2\text{O}$ 仅相差 4 个结晶水, 性质相近. 因此, 加入二乙醇胺后, 生成的 $(\text{Zn}(\text{OH})_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_3$ 可在 Ru-Zn(8.4%) 催化剂表面聚结成相.

2.1.4 XRF 结果

ZrO_2 及各使用后 Ru-Zn 催化剂中的金属含量列于表 2. 可以看出, 加氢后的样品主要含有 Ru, Zn, Zr 和 Hf 等元素, Hf 为 ZrO_2 中含有的共生氧化物 HfO_2 . 随着二乙醇胺用量的增加, 样品中的 Zn 含量逐渐增加. XRD 证实二乙醇胺能与浆液中的 ZnSO_4 反应生成难溶性 $(\text{Zn}(\text{OH})_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_3$, 后者极易化学吸附在催化剂表面, 且随着二乙醇胺用量的增加而增加, 从而导致催化剂 Zn 含量的增加. 值得强调的是, $(\text{Zn}(\text{OH})_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_3$ 是在反应过程中生成的, 它只能分散在催化剂表面上. 催化剂循环使用后 Ru 和 Zn 含量的减少同样使它有少量流失. 这与 XRD 结果一致. 添加 0.4 g 二乙醇胺的 Ru-Zn(4.9%) 催化剂和添加 0.3 g 二乙醇胺的 Ru-Zn(8.4%) 催化剂使用后的 Zn 含量分别达 6.15% 和 6.23%, 表明它们表面碱式硫酸锌盐含量最高, 与 XRD 结果一致.

表 2 不同量二乙醇胺作添加剂 Ru-Zn 催化剂加氢后样品中的金属元素含量

Table 2 Contents of metal elements in the catalyst samples with different diethanolamine dosages as an additive after the hydrogenation

Sample	Contents (%)			
	Ru	Zn	Zr	Hf
ZrO_2	—	—	94.65	5.35
Ru-Zn(4.9%)-0	17.15	2.91	76.44	3.51
Ru-Zn(4.9%)-0.2	16.67	3.60	76.47	3.25
Ru-Zn(4.9%)-0.3	17.28	4.56	74.90	3.26
Ru-Zn(4.9%)-0.4	16.62	6.15	74.25	2.98
Ru-Zn(4.9%)-R	9.32	3.42	82.81	3.45
Ru-Zn(8.4%)-0.3	17.32	6.23	73.98	2.47

2.1.5 FT-IR 结果

图 3 为不同二乙醇胺添加量时 Ru-Zn(4.9%) 催化剂使用后的 FT-IR 谱. 可以看出, 随着二乙醇胺量的增加, 加氢后催化剂上并未出现二乙醇胺的吸

图 3 不同量二乙醇胺作添加剂 Ru-Zn(4.9%) 催化剂加氢后样品的 FT-IR 谱

Fig. 3. FT-IR spectra of the Ru-Zn(4.9%) catalyst with different diethanolamine dosages as an additive after the hydrogenation.

图 4 不同量二乙醇胺作添加剂时 Ru-Zn(4.9%) 催化剂加氢后样品的 TPR 谱

Fig. 4. TPR profiles of the Ru-Zn(4.9%) catalyst with different diethanolamine dosages as an additive after the hydrogenation.

收峰. 这说明二乙醇胺存在于浆液中, 吸附在催化剂上的很少.

2.1.6 H₂-TPR 结果

图 4 为不同二乙醇胺添加量时 Ru-Zn(4.9%) 催化剂加氢后的 TPR 谱. 可以看出, 所有样品只有一个还原峰, 归属于 RuO_x 的还原. 这表明在洗涤过程中催化剂表面有一部分活性强的活性位被氧化了. 随着二乙醇胺量的增加, 还原峰向低温方向移动; 但至 0.4 g 时, 还原峰温度又有所升高. 虽然由 FT-IR 结果可知, 吸附在催化剂表面的二乙醇胺量很少, 但在浆液中存在的二乙醇胺由于空间效应可以抑制颗粒的聚结. 二乙醇胺用量越多, 加氢后催化剂的颗粒越小, 因此还原峰温度逐渐降低. 但当

二乙醇胺用量超过 0.4 g 时, (Zn(OH)₂)₃·(ZnSO₄)(H₂O)₃ 因含量太高而在催化剂表面聚结, 延缓了 RuO_x 的还原. 还可以看出, 所有样品还原结束的温度都小于反应温度 150 °C, 这表明在反应过程中催化剂中 Ru 是以金属态存在.

2.2 Ru-Zn 催化剂上苯选择加氢反应性能

2.2.1 二乙醇胺量对催化剂性能的影响

图 5 为不同量二乙醇胺作添加剂时 Ru-Zn(4.9%) 催化剂上苯选择加氢反应性能. 可以看出, 二乙醇胺用量由 0 g 增加至 0.3 g 时, 催化剂活性逐渐降低, 同一转化率下环己烯选择性升高, 在反应时间内最高环己烯收率由 55.2% 增至 59.4%. 二乙醇胺增加至 0.4 g 时, 催化剂活性显著降低, 而

图 5 不同量二乙醇胺作添加剂时 Ru-Zn(4.9%) 催化剂上苯加氢反应性能

Fig. 5. Reaction performance of benzene hydrogenation over Ru-Zn(4.9) catalyst samples with different diethanolamine dosages as an additive. Reaction conditions: 1.96 g catalyst, 9.8 g ZrO₂, 49.2 g ZnSO₄·7H₂O, $p(\text{H}_2) = 5 \text{ MPa}$, 150 °C.

同转化率下环己烯选择性却略有升高, 最高环己烯收率降至 41.9%。可见二乙醇胺用量为 0.3 g 时, Ru-Zn(4.9%) 催化剂上苯选择加氢反应性能最佳。由上文可知, 二乙醇胺与浆液中 ZnSO_4 反应生成的并化学吸附在催化剂表面的 $(\text{Zn}(\text{OH})_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_3$ 改变了催化剂的表面组成, 从而影响了催化剂性能。根据文献[1]报道, $(\text{Zn}(\text{OH})_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_3$ 的可能作用有: (1) 化学吸附在催化剂表面时含有大量的 Zn^{2+} , 后者可与环己烯形成一个稳定的配合物, 从而促进了环己烯从催化剂表面的脱附, 并抑制其再吸附, 因而提高环己烯的选择性; (2) 化学吸附在催化剂表面的 $(\text{Zn}(\text{OH})_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_3$ 可以占据不适宜环己烯选择加氢生成环己烯的活性位; (3) 化学吸附在催化剂表面的 $(\text{Zn}(\text{OH})_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_3$ 含有大量的结晶水, 可极大地增加催化剂的亲水性, 使环己烯的选择性提高; (4) $(\text{Zn}(\text{OH})_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_3$ 与活性组分 Ru 之间的相互作用可以改变 Ru 的电子结构, 使 Ru 催化剂适合苯选择加氢制环己烯^[2]。Struijk 等^[17]发现, 盐可选择性地化学吸附在一些最强的活性位上, 降低苯和环己烯的吸附焓, 提高环己烯的脱附速率, 从而降低了 Ru 催化剂的活性而提高环己烯的选择性。二乙醇胺用量的增加使得化学吸附在催化剂表面的 $(\text{Zn}(\text{OH})_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_3$ 量增加, 因此催化剂的活性降低, 而环己烯选择性升高。二乙醇胺为 0.3 g 时, $(\text{Zn}(\text{OH})_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_3$ 高度分散于催化剂和 ZrO_2 表面, 此时 Ru-Zn(4.9%) 催化剂不但具有较高的活性, 而且具有较高的选择性。此外, FT-IR 结

果表明化学吸附在催化剂表面的二乙醇胺量很少, 但存在于浆液的硫酸二乙醇胺盐中 O 或 N 孤电子对可以与环己烯形成氢键^[18], 从而可极大地稳定环己烯分子, 减小环己烯再吸附到催化剂表面进一步加氢生成环己烷的几率。 $(\text{Zn}(\text{OH})_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_3$ 和二乙醇胺盐协同作用是二乙醇胺提高 Ru-Zn 催化剂对环己烯选择性的主要原因。

2.2.2 不同 Zn 含量对催化剂性能的影响

在 0.3 g 二乙醇胺和其它反应条件相同的情况下, 考察 Zn 含量对 Ru-Zn 催化剂性能的影响, 结果示于图 6。可以看出, Ru-Zn(4.9%) 催化剂的活性和环己烯收率都比 Ru-Zn(8.4%) 催化剂高得多, 而相同苯转化率下后者的环己烯选择性却比前者高不到 2%。可见, Ru-Zn(4.9%) 催化剂性能明显优于 Ru-Zn(8.4%) 催化剂。加入 0.3 g 二乙醇胺后, 碱式硫酸锌盐在 Ru-Zn(8.4%) 催化剂表面聚集, 因而 Ru-Zn(8.4%) 催化剂的活性大幅度降低, 而环己烯选择性仅略有提高。二乙醇胺量为 0.3 g 时, 碱式硫酸锌盐在 Ru-Zn(4.9%) 催化剂表面上高度分散, 致使 Ru-Zn(4.9%) 催化剂的性能最佳。在该条件下, 反应 20 min 苯转化率为 71.3% 时, 环己烯选择性和收率分别为 78.9% 和 56.3%。这不但满足工业要求, 而且远远超过目前工业催化剂水平^[5,9]。同时也表明 Ru-Zn 催化剂最佳 Zn 含量与添加剂密切相关。

2.2.3 催化剂的稳定性

图 7 为 0.3 g 二乙醇胺作添加剂时 Ru-Zn(4.9%) 催化剂循环使用 5 次的催化性能。可以看出, 使用至第 4 次时, 反应 25 min 苯转化率和

图 6 二乙醇胺作添加剂时不同 Zn 含量催化剂的催化性能

Fig. 6. Catalytic performance of the Ru-Zn catalyst with different Zn contents for hydrogenation of benzene to cyclohexene. Reaction conditions: 1.96 g catalyst, 9.8 g ZrO_2 , 49.2 g $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, 0.3 g diethanolamine, $p(\text{H}_2) = 5 \text{ MPa}$, 150°C .

图 7 二乙醇胺作添加剂时 Ru-Zn(4.9%) 催化剂循环使用性能

Fig. 7. Reusability of the Ru-Zn(4.9%) catalyst for selective hydrogenation of benzene to cyclohexene. Reaction conditions: 1.96 g catalyst, 9.8 g ZrO_2 , 49.2 g $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, 0.3 g diethanolamine, $p(\text{H}_2) = 5$ MPa, 150 °C.

环己烯选择性仍能保持在 75% 以上, 环己烯收率为 58% 以上. 这表明 0.3 g 二乙醇胺作添加剂时 Ru-Zn(4.9%) 催化剂具有较好的稳定性. 循环使用至第 5 次时, 苯转化率、环己烯选择性和收率分别降为 59.8%, 80.4% 和 48.1%. XRD 和 XRF 结果可知, 这是由于循环使用过程催化剂损失所致. 值得一提的是, 在催化剂循环使用至第 3 次时, 苯转化率、环己烯选择性和收率分别达 84.3%, 75.5% 和 63.6%, 这是目前报道的最好结果^[3,7].

3 结论

二乙醇胺与浆液中的 ZnSO_4 反应生成 $(\text{Zn}(\text{OH})_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_3$ 和硫酸二乙醇胺盐, 分别化学吸附在催化剂表面和存在于浆液中, 二者间的协同作用显著提高了 Ru 基催化剂上苯选择加氢生成环己烯的选择性. 当二乙醇胺为 0.3 g 时, $(\text{Zn}(\text{OH})_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_3$ 在 Ru-Zn(4.9%) 催化剂和分散剂 ZrO_2 上高度分散, 环己烯选择性和催化剂稳定性均最佳. 这表明 Ru-Zn 催化剂中最佳 Zn 含量不仅与浆液中 ZnSO_4 浓度有关, 而且还与添加剂的种类有关.

参 考 文 献

- 1 孙海杰, 郭伟, 周小莉, 陈志浩, 刘仲毅, 刘寿长. 催化学报 (Sun H J, Guo W, Zhou X L, Chen Zh H, Liu Zh Y, Liu

Sh Ch. *Chin J Catal*), 2011, **32**: 1

- 2 孙海杰, 张旭东, 陈志浩, 周小莉, 郭伟, 刘仲毅, 刘寿长. 催化学报 (Sun H J, Zhang X D, Chen Zh H, Zhou X L, Guo W, Liu Zh Y, Liu Sh Ch. *Chin J Catal*), 2011, **32**: 224
- 3 Sun H J, Chen Zh H, Guo W, Zhou X L, Liu Zh Y, Liu Sh Ch. *Chin J Chem*, 2011, **29**: 369
- 4 Nagahara H, Ono M, Konishi M, Fukuoka Y. *Appl Surf Sci*, 1997, **121/122**: 448
- 5 吴济民, 杨炎峰, 陈聚良. 化工进展 (Wu J M, Yang Y F, Chen J L. *Chem Ind Eng Progr*), 2003, **22**: 295
- 6 Liu J L, Zhu L J, Pei Y, Zhuang J H, Li H, Li H X, Qiao M H, Fan K N. *Appl Catal A*, 2009, **353**: 282
- 7 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
- 8 Liu H Z, Liang S G, Wang W T, Jiang T, Han B X. *J Mol Catal A*, 2011, **341**: 35
- 9 孙海杰, 张程, 袁鹏, 李建修, 刘寿长. 催化学报 (Sun H J, Zhang Ch, Yuan P, Li J X, Liu Sh Ch. *Chin J Catal*), 2008, **29**: 441
- 10 Zhou X L, Sun H J, Guo W, Liu Z Y, Liu S C. *J Natur Gas Chem*, 2011, **20**: 53
- 11 刘寿长, 罗鸽, 谢云龙. 分子催化 (Liu Sh Ch, Luo G, Xie Y L. *J Mol Catal (China)*), 2002, **16**: 349
- 12 Nagahara H, Konishi M. US 4 734 536. 1988
- 13 Liu Sh Ch, Liu Zh Y, L, Wang Z, Zhao S H, Wu Y M. *Appl Catal A*, 2006, **313**: 49
- 14 Wang J Q, Wang Y Z, Xie S H, Qiao M H, Li H X, Fan K N. *Appl Catal A*, 2004, **272**: 29
- 15 Yuan P Q, Wang B Q, Ma Y M, He H M, Cheng Z M, Yuan W K. *J Mol Catal A*, 2009, **301**: 140
- 16 何惠民, 袁佩青, 马悦谔, 程振民, 袁渭康. 催化学报 (He H M, Yuan P Q, Ma Y M, Cheng Zh M, Yuan W K. *Chin J Catal*), 2009, **30**: 312
- 17 Struijk J, Moene R, van der Kamp T, Scholten J J F. *Appl Catal A*, 1992, **89**: 77
- 18 Fan G Y, Li R X, Li X J, Chen H. *Catal Commun*, 2008, **9**: 1394

英 译 文

English Text

The production of nylon-6 and nylon-66 from benzene and cyclohexene has attracted much attention for its atomic economy, mild reaction condition, and energy saving, and it is environmentally benign and is superior to the use of benzene and cyclohexane [1–3]. However, thermodynamics make it difficult to get cyclohexene from benzene hydrogenation because the standard free energy change for cyclohexene formation from benzene hydrogenation is -23 kJ/mol, while that for cyclohexane formation is -98 kJ/mol [1]. Hence, developing a catalyst with high selectivity to cyclohexene from benzene selective hydrogenation is the key

in this technology.

The hydrophilic modification of the catalyst surface with promoters or additives is an effective method to improve the cyclohexene selectivity of a Ru-based catalyst. In 1989, Asahi Chemical Industry Co. industrialized the process for producing cyclohexene from benzene selective hydrogenation by employing an unsupported Ru-Zn catalyst and obtained a cyclohexene yield of 32% at a benzene conversion of 40% [4,5]. Liu et al. [6] prepared a Ce-promoted Ru/SBA-15 catalyst by a "two solvents" impregnation method and achieved a cyclohexene yield of 53.8% over the RuCe/SBA-15 catalyst with a Ce/Ru molar ratio of 0.25 in the presence of ZnSO_4 (0.42 mol/L). They achieved a cyclohexene yield of 57% and a selectivity of 69% at the benzene conversion of 82% over a Ru-La/SBA catalyst with CdSO_4 and ZnSO_4 as co-modifiers [7]. Liu et al. [8] carried out the reaction over a Ru-Cu/ZnO catalyst with the Ru/Cu ratio of 10:1 in 2 ml of 0.3 mol/L NaOH solution and obtained a maximum cyclohexene yield of 49.4% at a benzene conversion of 72.3% and a cyclohexene selectivity of 68.3%. Although the cyclohexene yields over these promising catalysts were higher than that of the industrial catalyst, the corresponding selectivity for cyclohexene was lower than 70%, while a selectivity for cyclohexene close to 80% is required for industrial use to reduce the difficulties in subsequent product (including benzene, cyclohexene, and cyclohexane) separation.

In a previous work, we prepared a monolayer dispersed Ru-Zn catalyst and achieved a cyclohexene selectivity of 69.8% at a benzene conversion of 84.8% at 10 min reaction time [2]. In addition, we doped the Ru catalyst with Mn and Zn as co-promoters and obtained a cyclohexene selectivity of 81.1% at a benzene conversion of 60.2% at 20 min reaction time over the Ru-Mn-Zn catalyst with the Mn/Zn ratio of 0.3 and the addition of 0.5 g NaOH. A maximum cyclohexene yield of 59.9% was also achieved at 20 min [10]. We also briefly reported cyclohexene yields of 61.4% and 58.9%, respectively, with PEG-20000 and diethanolamine as additives on a Ru-Zn catalyst [3]. In this work, the influence of the diethanolamine doses on the performance of the Ru-Zn catalyst for benzene selective hydrogenation to cyclohexene was investigated in the presence of ZnSO_4 . The catalyst before and after hydrogenation was characterized and the role of diethanolamine is discussed.

1 Experimental

1.1 Catalyst preparation

The Ru-Zn catalysts were prepared according to the procedure in the literature [11]. The required amounts of $\text{RuCl}_3 \cdot \text{H}_2\text{O}$ and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ were dissolved in 200 ml H_2O

with agitation. To the stirred solution, 200 ml of 30% NaOH solution was added rapidly and the resulting mixture was agitated for an additional 4 h at 80 °C. The mixture was left to stand and the black precipitate obtained was washed three times with an aqueous solution of 5% NaOH after the supernatant had been removed by decantation. This black precipitate was dispersed in 400 ml of 5% NaOH solution and charged into a 1 L autoclave lined with Teflon. Hydrogen was introduced into the autoclave to a pressure of 5 MPa and the reduction was conducted at 150 °C and 800 r/min stirring for 3 h. The reaction mixture was cooled and the black powder obtained was washed three times with 5% NaOH and then with water until neutral, and the desired Ru-Zn catalyst was obtained. The amounts of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ were adjusted to give the desired Zn loadings. The catalysts with different Zn loadings were denoted Ru-Zn(*x*), where *x* is the Zn loading determined by atomic absorption spectroscopy (AAS).

1.2 Catalyst characterization

AAS for determining the Zn loading was performed on a Perkin Elmer AAnalyst 300 instrument operated at $\lambda = 213.9$ nm and slit width = 0.20 nm. N_2 physisorption (BET) was determined on a Quantachrome Nova 100e apparatus. Transmission electron microscopy (TEM) was carried out a JEOL JEM-2100 instrument. X-ray diffraction (XRD) patterns were acquired on a PANalytical X'Pert PRO instrument using $\text{Cu } K_\alpha$ ($\lambda = 0.1541$ nm) in a scan range of 5°–90° at a scan step of 0.03°. The elemental analysis was measured by X-ray fluorescence (XRF) on a Bruker S4 Pioneer instrument. Fourier transform infrared (FT-IR) spectra were recorded using a KBr pellet on a Thermo Nicolet Nexus-470 spectrophotometer. H_2 temperature-programmed reduction (H_2 -TPR) was carried out on a homemade microreactor with a thermal conductivity detector (TCD). The flow rate of 5% H_2 - N_2 was 30 ml/min and the heating rate was 10 °C/min.

1.3 Catalyst test

The selective hydrogenation of benzene was performed in a 1 L autoclave lined the Hastelloy. The autoclave was charged with 280 ml H_2O containing 1.96 g catalyst, 9.8 g ZrO_2 , 49.2 g $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, and a desired amount of diethanolamine. This was heated at H_2 pressure of 5 MPa and stirring rate of 800 r/min. Benzene (140 ml) was fed in and the stirring rate was increased to 1400 r/min to exclude diffusional effects when the temperature reached 150 °C. The reaction products were monitored by taking a small amount of the reaction mixture every 5 min for analysis using a GC-1690 gas chromatograph with an FID detector, which purchased from Hangzhou Kexiao Instrument Co. Benzene conversion and cyclohexene selectivity were calculated

based on the product concentration calculated using corrected peak area normalization. At the end of the reaction, the organic phase was removed using a separator funnel. The slurry containing the mixture of the catalyst and ZrO_2 was reused using the above operation without any addition. After the reaction, the organic liquid was removed and the solid sample was washed for characterization. The samples after reaction and recycle were denoted Ru-Zn(x)-y and Ru-Zn(x)-R, respectively, where y and R represent the mass of diethanolamine and recycle time, respectively.

2 Results and discussion

2.1 Catalyst characterization

2.1.1 N_2 physisorption

Table 1 shows the textural properties of ZrO_2 , Ru-Zn(4.9%) catalyst, and the samples with different diethanolamine doses as additives after reaction. The Ru-Zn(4.9%) catalyst has a specific surface area of $62 \text{ m}^2/\text{g}$, pore diameter of 5.74 nm, and pore volume of $0.089 \text{ cm}^3/\text{g}$. The specific surface area, pore diameter, and pore volume of the samples after reaction and recycles were close to those of ZrO_2 , which may be related to the dosage of ZrO_2 (mass ratio of ZrO_2 and catalyst was 5:1).

2.1.2 TEM results

Figure 1 gives the TEM images of the Ru-Zn(4.9%) catalyst and the samples after reaction and recycles using 0.3 g diethanolamine as an additive, and the crystallite size distribution of the corresponding catalyst. From Fig. 1, the crystallite size of the Ru-Zn(4.9%) catalyst was 3.5 nm. Figure 1 shows that the catalyst particles were separated and isolated. This suggests that a suitable amount of ZrO_2 can remarkably suppress agglomeration that could have occurred due to the collision of different particles under high agitation. The added ZrO_2 also reduced catalyst adhesion to the metallic surface of the reactor [12]. In addition, a suitable amount of ZrO_2 improved the activity and selectivity of the catalyst [13]. As can be seen from Fig. 1, the crystallite size of the catalyst after the first hydrogenation run was 3.5 nm, which agrees with that of the fresh catalyst. The crystallite size of the catalyst after five recycles was slightly increased to 3.8 nm. The main component of the Ru-Zn catalyst is metallic Ru, which is difficult to disperse and prone to agglomerate to form bigger particles. The very slight increase of the catalyst size after five recycles confirmed the dispersion effect of ZrO_2 .

2.1.3 XRD results

Figure 2 shows XRD patterns of the Ru-Zn(4.9%) catalyst and the catalyst after hydrogenation with different diethanolamine dosages as additives. The reflections at $2\theta = 38.4^\circ$, 42.4° , 43.9° , 58.3° , 69.3° , and 78.3° were assigned to metallic Ru (JCPDS 01-070-0274). Sun et al. [2] has used XRD and XPS to confirm that most of the Zn species in Ru-Zn catalysts exist as ZnO. Part of the Zn in the catalyst was present in the form of metallic Zn. However, no ZnO or metallic Zn diffractions were detected in the XRD patterns, indicating their high dispersion and that their small crystallite size was smaller than the detectable limit of the instrument. When the diethanolamine dosage was increased from 0 to 0.3 g, besides the weak diffraction at $2\theta = 43.9^\circ$ from the Ru-Zn(4.9%) catalyst after hydrogenation due to metallic Ru (JCPDS 01-070-0274), the other diffractions corresponded to the monoclinic phase of ZrO_2 (JCPDS 00-024-1165). When the diethanolamine dosage was 0.4 g, in addition to the diffractions of metallic Ru and ZrO_2 , the diffraction at $2\theta = 9.8^\circ$ from the Ru-Zn(4.9%) catalyst after hydrogenation was attributed to the $(\text{Zn}(\text{OH})_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_3$ phase (JCPDS 01-078-0247). This revealed that the diethanolamine added reacted with ZnSO_4 in the slurry to form an insoluble $(\text{Zn}(\text{OH})_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_3$ salt and diethanolamine sulfate. This is shown as reactions (1) and (2):

This also indicated that the $(\text{Zn}(\text{OH})_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_3$ salt was highly dispersed on the Ru-Zn(4.9%) catalyst and ZrO_2 particles when the dosage of diethanolamine was 0.3 g. It was found that the diffraction at $2\theta = 43.9^\circ$ corresponding to metallic Ru was remarkably weakened after five recycles, indicating a loss of catalyst in the oil phase when this phase was separated from the catalyst during the recycling. It was observed that the diffraction at $2\theta = 9.8^\circ$ from the $(\text{Zn}(\text{OH})_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_3$ phase also appeared with the Ru-Zn(8.4%) catalyst after hydrogenation when the dosage of diethanolamine was 0.3 g. It was reported that part of the Zn species in the Ru-Zn(8.6%) catalyst existed as ZnO and ZnO can react with ZnSO_4 in the slurry to form an insoluble $\text{ZnSO}_4 \cdot 3\text{Zn}(\text{OH})_2 \cdot 7\text{H}_2\text{O}$ salt (JCPDS 00-009-0204), which can be dispersed on catalyst surface to form a monolayer [2]. Diethanolamine also can react with ZnSO_4 in the slurry to form a $(\text{Zn}(\text{OH})_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_3$ salt, with properties close to those of the $\text{ZnSO}_4 \cdot 3\text{Zn}(\text{OH})_2 \cdot 7\text{H}_2\text{O}$ salt since their difference is only four water molecules of crystallization. Thus, with the addition of diethanolamine, the $(\text{Zn}(\text{OH})_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_3$ formed can constitute a phase with the ZnSO_4 .

$3\text{Zn}(\text{OH})_2 \cdot 7\text{H}_2\text{O}$ salt on the Ru-Zn(8.4%) catalyst surface.

2.1.4 XRF results

Table 2 gives the amounts of the metallic elements of ZrO_2 and the Ru-Zn catalysts before and after hydrogenation with different diethanolamine dosages as additives. The sample after hydrogenation mainly contains four metallic elements, Ru, Zn, Zr and Hf. Hf comes from the ZrO_2 sample that contains HfO_2 . The amount of Zn in the Ru-Zn(4.9%) catalyst after hydrogenation increased with increasing diethanolamine dosages. XRD confirmed that diethanolamine reacted with ZnSO_4 in the slurry to form an insoluble $(\text{Zn}(\text{OH})_2)_3(\text{ZnSO}_4) \cdot (\text{H}_2\text{O})_3$ salt that was easily adsorbed on the catalyst surface. This resulted in the increase of the Zn content in the samples. It is to be noted that the $(\text{Zn}(\text{OH})_2)_3(\text{ZnSO}_4) \cdot (\text{H}_2\text{O})_3$ salt was formed in the hydrogenation process and so can only be dispersed on the catalyst surface. It was found that both Ru and Zn contents decreased after five recycles, which indicated the loss of catalyst in the recycles. This was consistent with the XRD results. The Zn contents in the Ru-Zn(4.9%) catalyst with 0.4 g diethanolamine and the Ru-Zn(8.4%) catalyst with 0.3 g diethanolamine after hydrogenation were 6.15% and 6.23%, respectively, which showed the high content of the $(\text{Zn}(\text{OH})_2)_3(\text{ZnSO}_4) \cdot (\text{H}_2\text{O})_3$ salt on the catalyst surface. This was in agreement with the XRD results.

2.1.5 FT-IR results

Figure 3 shows the FT-IR spectra of the Ru-Zn(4.9%) catalyst after hydrogenation with different diethanolamine dosages as additives and that of diethanolamine as a reference. With the increase of diethanolamine dosages, no absorbance from diethanolamine was observed on the catalysts after hydrogenation, which indicated that diethanolamine was not adsorbed on the catalyst surface and the diethanolamine existed in the slurry.

2.1.6 H_2 -TPR results

Figure 4 gives the H_2 -TPR profiles of the Ru-Zn(4.9%) catalyst after hydrogenation with different diethanolamine dosages as additives. All the samples have one reduction peak due to the reduction of RuO_x , indicating the oxidation of the most active Ru sites during catalyst washing. With the increase of the diethanolamine dosage, the reduction peak shifted to lower temperatures. However, on further increasing the diethanolamine dosage, the reduction peak shifted back. Although the FT-IR spectra revealed that little diethanolamine was adsorbed on the catalyst surface, diethanolamine in the slurry can suppress agglomeration of the catalyst

due to a space effect. Therefore, with increasing diethanolamine dosage, the catalyst particles after hydrogenation became smaller, which lead to the reduction peak shifting to lower temperatures. However, when the diethanolamine dosage increased to 0.4 g, too much $(\text{Zn}(\text{OH})_2)_3 \cdot (\text{ZnSO}_4) \cdot (\text{H}_2\text{O})_3$ salt was formed and deposited on the catalyst surface, which made the reduction of RuO_x more difficult. It is also found that the temperatures for the full reduction of the samples were all lower than the reaction temperature of 150 °C, implying the existence of metallic Ru during the reaction.

2.2 Catalytic performance

2.2.1 Effect of diethanolamine dosages on catalytic activity

Figure 5 shows the activity of the Ru-Zn(4.9%) catalyst with different diethanolamine dosages as additives. With increasing diethanolamine dosage from 0 to 0.3 g, the activity of the catalyst decreased, the cyclohexene selectivity increased for the same benzene conversion, and the maximum yield of cyclohexene increased to 59.4% from 55.2% with reaction time. Increasing diethanolamine dosage to 0.4 g, the activity of the catalyst was significantly decreased, but the cyclohexene selectivity was slightly increased at the same benzene conversion and the maximum yield of cyclohexene decreased to 41.9%. The Ru-Zn(4.9%) catalyst exhibited the best performance for benzene selective hydrogenation to cyclohexene at the optimum diethanolamine dosage of 0.3 g. As known from the above characterization, diethanolamine can react with ZnSO_4 to form an insoluble $(\text{Zn}(\text{OH})_2)_3(\text{ZnSO}_4) \cdot (\text{H}_2\text{O})_3$ salt. This adsorbed salt changed the composition of the catalyst surface, which is a vital factor in the performance of the catalyst. Based on previous works [7], the insoluble $(\text{Zn}(\text{OH})_2)_3(\text{ZnSO}_4) \cdot (\text{H}_2\text{O})_3$ salt may play four roles as follows. (1) The $(\text{Zn}(\text{OH})_2)_3(\text{ZnSO}_4) \cdot (\text{H}_2\text{O})_3$ salt contains large amounts of Zn^{2+} ions. The Zn^{2+} ions can form a stable complex with cyclohexene, which can accelerate the desorption of cyclohexene and retard the re-adsorption of the desorbed cyclohexene [7]. This improved the selectivity for cyclohexene. (2) The $(\text{Zn}(\text{OH})_2)_3(\text{ZnSO}_4) \cdot (\text{H}_2\text{O})_3$ salt adsorbed on the catalyst surface can block active sites unsuitable for the formation of cyclohexene. Struijk et al. [17] suggested that the salt can selectively cover the most reactive sites, which lowers the adsorption enthalpies of benzene. This resulted in an increase of the cyclohexene desorption rate, which enhances the selectivity for cyclohexene. (3) The $(\text{Zn}(\text{OH})_2)_3(\text{ZnSO}_4) \cdot (\text{H}_2\text{O})_3$ salt adsorbed on the catalyst surface comprised plentiful water of crystallization, which can enhance the hydrophilicity of the catalyst and improve the selectivity to cyclohexene. (4) An interaction between the $(\text{Zn}(\text{OH})_2)_3(\text{ZnSO}_4) \cdot (\text{H}_2\text{O})_3$ salt and the active Ru component

can modify the electronic structure of Ru, which makes the Ru catalyst more suitable for benzene selective hydrogenation to cyclohexene [2]. Therefore, with the increase of dithanolamine dosage, the amount of the $(\text{Zn}(\text{OH})_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_3$ salt increased, resulting in the increase of the activity and the decrease of the selectivity for cyclohexene. When the dithanolamine dosage was 0.3 g, the $(\text{Zn}(\text{OH})_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_3$ salt was highly dispersed on the surface of the Ru-Zn(4.9%) catalyst and the catalyst exhibited good activity and excellent selectivity for cyclohexene. FT-IR confirmed that little dithanolamine was adsorbed on the catalyst surface. The isolated electron pair of O (or N) of dithanolamine sulfate can form a hydrogen bond, which can significantly stabilize cyclohexene and reduce the re-adsorption of desorbed cyclohexene onto the catalyst and its further hydrogenation from cyclohexene to cyclohexane [18]. Thus the synergism of $(\text{Zn}(\text{OH})_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_3$ and diethanolamine sulfate improved the cyclohexene selectivity of the Ru-Zn catalyst.

2.2.2 Effect of Zn content on catalytic performance

With 0.3 g dithanolamine, the effect of the Zn content on the performance of the Ru-Zn catalysts was investigated. The results are shown in Fig. 6. Both the activity and cyclohexene yield of the Ru-Zn(4.9%) catalyst were higher than the Ru-Zn(8.4%) catalyst, but the selectivity of the latter was higher although by less than 2%. Obviously, the performance of the Ru-Zn(4.9%) catalyst was superior to that of the Ru-Zn(8.4%) catalyst. With the addition of 0.3 g dithanolamine, the $(\text{Zn}(\text{OH})_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_3$ salt agglomerated on the Ru-Zn(8.4%) catalyst, which led to a decrease of the activity of the catalyst and a slight increase of the selectivity for cyclohexene. When the dithanolamine dosage was 0.3 g, the $(\text{Zn}(\text{OH})_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_3$ salt was highly dispersed on the Ru-Zn(4.9%) catalyst and this catalyst gave the best performance for benzene selective hydrogenation to cyclohexene. A selectivity for cyclohexene of 78.9% and a yield of 56.3% at a benzene conversion of 71.3% were obtained at 20

min reaction time under this condition. This not only meets the industrial requirement but also exceeds those of the industrial catalyst [5,9]. In addition, this also confirmed that the optimum Zn content of the Ru-Zn catalyst is closely related to the kind of additives.

2.2.3 Catalyst stability

Figure 7 shows the performance of Ru-Zn(4.9%) during five recycles with 0.3 g dithanolamine as an additive. Benzene conversion and cyclohexene selectivity were stable above 75% and cyclohexene yields were kept above 58% over the Ru-Zn(4.9%) catalyst in first four recycles. This demonstrated the good activity and selectivity as well as the excellent stability of the catalyst. However, the benzene conversion, cyclohexene selectivity, and yield decreased to 59.8%, 80.4%, and 48.1% in the fifth recycle, respectively. XRD and XRF results revealed that the decrease was caused by the loss of catalyst in the recycling. It is worth noting that the benzene conversion, cyclohexene selectivity, and cyclohexene yield reached 84.3%, 75.5%, and 63.6%, respectively, which is better than the best result previously [3,7].

3 Conclusions

Dithanolamine can react with ZnSO_4 to form an insoluble $(\text{Zn}(\text{OH})_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_3$ salt and diethanolamine sulfate. The synergism of the $(\text{Zn}(\text{OH})_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_3$ salt and diethanolamine sulfate improved the selectivity to cyclohexene of the Ru-based catalyst. When the diethanolamine dosage was 0.3 g, the $(\text{Zn}(\text{OH})_2)_3(\text{ZnSO}_4)(\text{H}_2\text{O})_3$ salt was highly dispersed on the Ru-Zn(4.9%) catalyst and the ZrO_2 particles and the catalyst exhibited excellent selectivity to cyclohexene and good stability. The optimum Zn content of the Ru-Zn catalyst depended on the concentration of ZnSO_4 in the slurry and also the kind of additives.

Full-text paper available online at Elsevier ScienceDirect
<http://www.sciencedirect.com/science/journal/18722067>