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非晶态合金 Ru 基催化剂在苯选择加氢中的应用进展

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摘要: 化学还原法制备的非晶态合金 Ru 基催化剂融合了纳米粒子和非晶态合金的结构特征, 在苯选择加氢反应中表现出高活性和高环己烯选择性; 尤其是负载型非晶态合金 Ru 基催化剂, 具有贵金属利用率高和易于工业化等优点, 有着明显的竞争优势. 本文综述了苯选择加氢的热力学和动力学特征, 非晶态合金催化剂结构和组成及其对催化性能的影响; 总结了催化工艺条件、催化剂可调变性和中试成果, 并展望了该技术的发展趋势.

关键词: 苯; 选择加氢; 环己烯; 非晶态合金; 钌基催化剂

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Progress in Ru-Based Amorphous Alloy Catalysts for Selective Hydrogenation of Benzene to Cyclohexene

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Abstract: Ru-based amorphous alloy catalysts prepared by the chemical reduction method have high activity and excellent cyclohexene selectivity due to their structure that has the merits of amorphous alloys and nano-particles. In particular, the supported catalysts have the advantages of better utilization of the Ru noble metal and ease of use in industry. The thermodynamics and kinetics for selective hydrogenation of benzene to cyclohexene over these catalysts, and the influence of the structure and composition of the catalysts were described. The reaction conditions, ability to modify the catalysts, and results of pilot tests were emphasized. Directions in this field for future research were suggested.

Key words: benzene; selective hydrogenation; cyclohexene; amorphous alloy; ruthenium-based catalyst

由苯出发经环己烯制备尼龙 6 和尼龙 66 比经环己烷的路线具有安全、节能和环境友好等特点, 一直为人们所关注[1~9]. 1989 年, 日本旭化成公司利用无负载 Ru-Zn 催化剂率先实现了苯选择加氢工业化[10]; 该催化剂具有高活性和高选择性等优点, 但催化剂效率, 即单位质量的 Ru 利用率低, 价格昂贵, 耐 S, Cl 和 Fe 等能力较差[11]. 迄今为止, 旭化成不对外转让催化剂制备技术. 20 世纪 90 年代, 我国开始研究并相继开发了苯选择加氢新型催化剂和催化工艺[12~16]. 其中以负载型非晶态合金催化剂最为突出. 非晶态合金具有“长程无序”、“短程有序”的结构和丰富的表面缺陷, 因此具有高的催化活性和特殊的选择性[17]; 自 1981 年文献[18]首次报道以来一直是催化材料研究的热点. 1999 年, Xie 等[19]用化学还原法制备了非晶态合金 Ru-B 催化剂, 并将其用于苯选择加氢制环己烯反应中, 环己烯收率达 31.2%; 引起了人们极大关注, 并使其成为苯选择加氢催化剂新材料开发的一个热点. 郑州大学[20,21]、复旦大学[22]、中国科学院大连化学物理研究所[23]和中国石油化工科学研究院[24]等单位相继申报了苯选择加氢制环己烯非晶态合金催化剂的制备专利. 本文综述了苯选择加氢制环己烯非晶态合金催化剂的研究进

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展, 尤其是郑州大学在该领域所取得的研究成果.

1 苯选择加氢制环己烯的热力学和动力学

苯选择加氢生成环己烯的标准 Gibbs 自由能变为–23 kJ/mol, 而苯完全加氢生成环己烷的则为–98 kJ/mol. 这表明苯选择加氢制环己烯反应在热力学上是极为不利的. 目前普遍认可的苯加氢机理为 Prasad 等[25]提出的两历程反应模型: (1) 分步加氢, 即苯经由环己二烯、环己烯到环己烷; (2) 苯一步加氢生成环己烷. 因此, 要有效实现苯选择加氢制环己烯, 必须抑制环己烯的继续加氢和苯的一步完全加氢. 为达到这一目的催化剂的亲水性修饰是重要途径之一. 这由 Struijk 等[5,6]最先提出, 现已被环己烯收率与催化剂载体亲水性密切相关的实验事实所证实[26,27]. 同时, 苯和环己烯在水溶液中溶解特性也证实了这一点. 苯在水中的溶解度为 125 mol/m^3, 是环己烯 (21 mol/m^3) 的 6 倍, 因此, 催化剂表面形成的滞水层有利于增加苯的浓度, 进而可促使环己烯脱附. 同时, 环己烯在水中溶解度较低, 而催化剂周围存在滞水层, 有利于阻止环己烯加氢生成环己烷 (见图 1). 该经验是苯选择加氢制环己烯催化剂开发的一个最重要的指导性原则.

本课题组在忽略苯一步加氢生成环己烷 (三分子反应几率很小) 的基础上, 推导出 Ru-Zn-B/ZrO$_2$ 催化剂上选择加氢制环己烯反应的动力学方程[28]. 低压下,

$$\frac{\mathrm{d}c(\mathrm{HE})}{\mathrm{d}t}=-\frac{\mathrm{d}c(\mathrm{BZ})}{\mathrm{d}t}+\frac{\mathrm{d}c(\mathrm{HE})}{\mathrm{d}t}=k_1c(\mathrm{BZ})p^2(\mathrm{H_2})-k_2p^2(\mathrm{H_2}) \qquad (1)$$

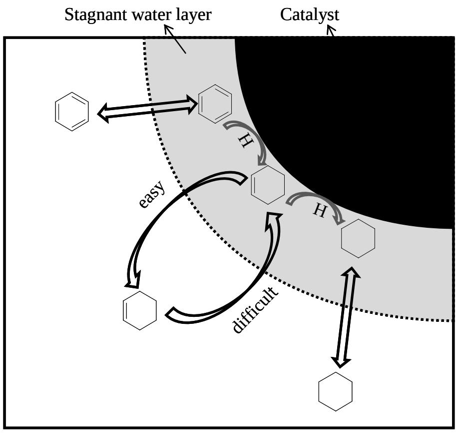

图 1 催化剂表面滞水层对苯加氢反应的影响

Fig. 1. Effect of the stagnant water layer on benzene hydrogenation.

中压下,

$$\frac{\mathrm{d}c(\mathrm{HE})}{\mathrm{d}t}=-\frac{\mathrm{d}c(\mathrm{BZ})}{\mathrm{d}t}+\frac{\mathrm{d}c(\mathrm{HE})}{\mathrm{d}t}=\frac{k_1c(\mathrm{BZ})\sigma p^2(\mathrm{H_2})}{1+\sigma p^2(\mathrm{H_2})}-\frac{k_2\sigma p^2(\mathrm{H_2})}{1+\sigma p^2(\mathrm{H_2})} \qquad (2)$$

高压下,

$$\frac{\mathrm{d}c(\mathrm{HE})}{\mathrm{d}t}=-\frac{\mathrm{d}c(\mathrm{BZ})}{\mathrm{d}t}+\frac{\mathrm{d}c(\mathrm{HE})}{\mathrm{d}t}=k_1c(\mathrm{BZ})-k_2 \qquad (3)$$

式中 HE 代表环己烯, BZ 代表苯.

将上述微分方程简化后积分, 计算得到的各种物质浓度与实验值基本吻合. 由上述动力学方程不难看出, 中间产物环己烯继续加氢对环己烯的反应级数为 0; 对氢的反应级数在低压下为 2, 中压下为 0~1, 高压下为 0. 这说明在该催化剂上环己烯极易吸附, 呈表面饱和状态. 氢的吸附则与压力有关, 只有在足够高的氢压下吸附才达饱和状态, 因此苯选择加氢一般在 5.0 MPa 的压力下进行. 要提高环己烯选择性, 就要设法增大 k_1, 降低 k_2. 亲水性的催化剂或加入能提高催化剂表面亲水性的物质可增大 k_1 和降低 k_2.

2 非晶态 Ru 基合金催化剂的结构和组成

2.1 纳米非晶态结构效应

Xie 等[19]指出, 非晶态 Ru-B/SiO$_2$ 催化剂活性和环己烯选择性都比晶态催化剂的高, 这归结于非晶态的结构效应. 本课题组采用化学还原法制备了 Ru-M-B/ZrO$_2$ (M = Zn,Co 和 Fe 等) 纳米非晶态合金催化剂, 活性组分 Ru 的微晶尺寸为 3.6~5.3 nm[29,30]; 其透射电镜 (TEM) 和选区电子衍射 (SAED) 照片见图 2. 在 Ru-Fe-B/ZrO$_2$ 催化剂上反应 25 min, 苯转化率为 54.8%, 环己烯选择性为 80.0%. 作者认为, 该催化剂高活性高选择性的主要原因在于它融合了纳米和非晶材料的特性. Bu 等[8]在 Ru 微晶尺寸为 5.6 nm 的 Ru-Ba/SBA-15 催化剂上获得了最高的环己烯收率; 他们认为具有该大小 Ru 微晶的催化剂表面含有最高浓度的适合环己烯生成的活性位. Nagahara 等[10]报道的 Ru-Zn 催化剂上 Ru 微晶尺寸约为 5 nm. 由此可见, 纳米和非晶态结构效应在苯选择加氢催化剂中起着关键作用.

2.2 非晶态合金催化剂中 B 的作用

Xie 等[19]采用浸渍-化学还原法制备了 Ru-B/

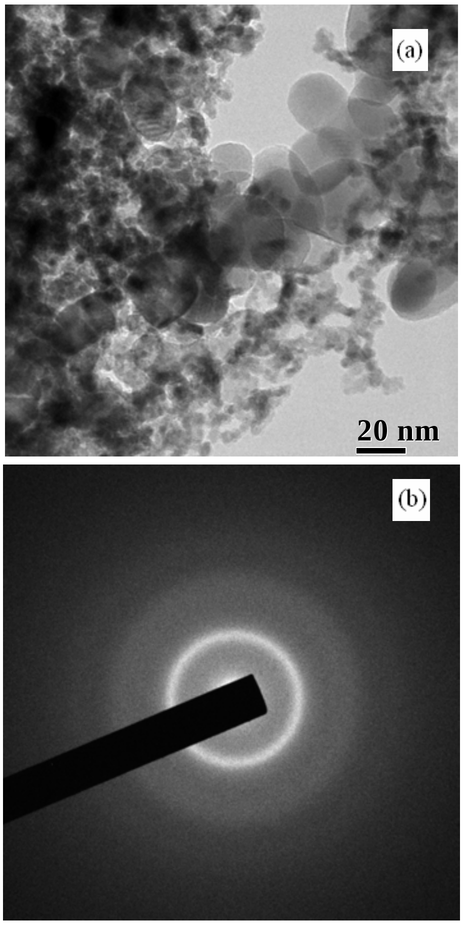

图 2 Ru-Fe-B/ZrO_2 催化剂的 TEM 和 SAED 照片

Fig. 2. TEM (a) and SAED (b) images of Ru-Fe-B/ZrO_2 catalyst.

SiO_2催化剂, 其催化苯选择加氢活性 (3.2%/(g·h)) 和环己烯选择性 (49.7%) 均比用 H_2 还原制得的 Ru 负载量相同的 Ru/SiO_2 的活性 (2.3%/(g·h)) 和选择性 (22.2%) 高. X 射线光电子能谱 (XPS) 和 Ar^+ 刻结果表明, 元素 B 在 Ru-B/SiO_2 催化剂中以游离态和氧化态两种形式存在, 且 B 在催化剂表面富集, 游离态 B 部分电子向 Ru 转移, 使得 Ru 富电子. 他们认为, B 对催化剂表面亲水性的修饰是 Ru-B/SiO_2 催化剂表现出高活性和高选择性的重要原因. 氧化态的 B 分散在催化剂表面, 与 H_2O 分子形成分子间氢键; 游离态的 B 由于部分电子向 Ru 转移, B 缺电子, 易与 H_2O 中的孤对电子成键. 因此, 催化剂表面亲水性增加, 环己烯选择性升高. Liu 等[31]采用化学还原法在不同还原温度下制备了一系列不同 B 含量的 Ru-B 催化剂, 发现当 B 含量由 0 增加到 10.1% 时, 环己烯收率从 6.3% 升高到 30.4%, 环己烯选择性从 19.4% 升高到 50.8% (见表 1). 这说明通过改变 Ru-B 非晶态合金中的 B 含量可显著改变催化剂的活性和选择性. 除还原温度外, 还原 pH 值[32], $NaBH_4$ 浓度和滴加速率[30,33~35]等也可调变非晶态合金催化剂中 B 的含量. 因此, 制备非晶态合金催化剂时需特别注意这些制备条件.

表 1 B 含量对非晶态合金 Ru-B 催化剂上苯加氢制环己烯反应的影响

Table 1 Influence of B content on the benzene hydrogenation to cyclohexene over the amorphous alloy Ru-B catalysts samples[31]

Alloy composition	Time (min)	X_{BZ}/%	S_{HE}/%	Y_{HE}/%
Ru	90	32.5	19.4	6.3
$Ru_{0.981}B_{0.019}$	55	28.1	25.3	7.1
$Ru_{0.958}B_{0.042}$	65	40.8	33.6	13.7
$Ru_{0.933}B_{0.067}$	85	55.7	39.0	21.7
$Ru_{0.916}B_{0.084}$	85	60.4	45.4	27.4
$Ru_{0.899}B_{0.101}$	75	59.9	50.8	30.4
$Ru_{0.901}B_{0.099}$	70	61.1	51.1	31.2

Rection conditions: benzene 35 ml, H_2O 100 ml, $ZnSO_4·7H_2O$ 1.5 g, Ru-B powder 0.15 g, 150 ℃, $p(H_2)$ = 4 MPa.

X_{BZ}: Benzene conversion; S_{HE}: Cyclohexene selectivity; Y_{HE}: Cyclohexene yield. The same below.

2.3 助剂的作用

研究表明, 助剂 Fe, Zn, La, Ce 和 Co 等, 在一定含量范围内, 有的能降低活性提高环己烯选择性; 有的既能提高催化剂活性, 又能提高催化剂选择性, 制备条件不同, 其影响略有差异[36~42]. 助剂一般有两种, 分为电子助剂和结构助剂. Fan 等[36]制备了 Ru-Co-B/γ-Al_2O_3 催化剂, XPS 和程序升温还原 (TPR) 结果表明, Co 以氧化态存在, 部分电子由 Ru 向 Co 转移, $Ru^{\delta+}$物种的形成导致 Ru(III) 的还原峰面积明显减小, 并认为由于 $Ru^{\delta+}$物种上环己烯吸附能力较差易脱附, 因而有利于环己烯选择性的提高. 本课题组研究发现, Ru-La-B/ZrO_2 催化剂中的 La 也以氧化态存在, 部分电子由 La 向 Ru 转移, 且随着加氢时间的延长, La 可被还原为金属[37,38]. 我们还发现, 能提高环己烯选择性的助剂多为过渡金属, 它们自身虽然没有催化加氢能力, 但由于它们具有空的 *d* 轨道, 能与环己烯的 π 键发生作用, 可从 Ru 上争夺环己烯, 使之一旦生成, 就易从催化剂表面脱附[39~41]. 这都证实助剂与 Ru 之间存在着电子作用, 从而影响着催化剂的活性和选择性. 同时有些助剂还起着结构助剂的作用: (1) 提高活性组分的分散度, 抑制 Ru 活性组分聚结[36]; (2) 占据一部分环己

烯快速加氢的活性位, 提供一个不适宜环己烯继续加氢的微环境[36,40]; (3) 提高Ru-B/ZrO$_2$非晶合金的稳定性, 延缓非晶晶化[42]; (4) 使Ru-B组分分布均匀, 活性组分处于比较均一的配位环境中[42].

助剂前体及其分布, 以及还原过程中NaOH残留也影响催化剂的性能. 本课题组在Ru-Fe-B/ZrO$_2$催化剂中加入Cu, 制备了双助剂催化剂; 结果发现催化剂的活性没有降低, 环己烯选择性反而略有提高[43]. 另外, CuCl$_2$·2H$_2$O作为助剂前体比CuSO$_4$·5H$_2$O具有更好的促进作用. 这可能是Cl$^-$优先占据了催化剂上吸附环己烯能力强的活性位, 有利于环己烯的脱附, 因而环己烯选择性升高. 另一方面, 吸附在催化剂表面的Cl$^-$能够以氢键的形式与H$_2$O分子键合, 使催化剂的表面亲水性增强, 从而提高了环己烯选择性; 而SO$_4^{2-}$则不具备这种作用. 秦会安等[41]制备了无负载Ru-Zn-B催化剂, 发现加料方式影响Zn在催化剂上的分布. 他们认为, 反加法由于自始至终NaBH$_4$溶液的量大大超过Ru^{3+}和Zn^{2+}被还原所需要的量, 从而确保Ru和Zn同时被还原, 各组分之间比较均匀, 因此苯转化率和环己烯选择性均较高. 而正加法Ru^{3+}先于Zn^{2+}被还原, 部分Ru活性位被Zn所覆盖, 导致催化剂活性明显降低. 文献[30,41]还考察了NaOH残留对催化剂性能的影响, 发现洗涤后滤液pH = 8或7.5 (即催化剂中有少量NaOH残留时), 催化剂具有优良的催化性能. 我们认为, 碱的残留起到了电子助剂的作用, 同时增加了催化剂表面的亲水性, 并且很容易与反应浆液中的Zn^{2+}生成微量的Zn(OH)$_2$. 二者都有利于提高环己烯选择性. 不同助剂对非晶态合金催化剂性能的影响示于表2.

2.4　载体的作用

Wang等[27]采用共沉淀-结晶-还原法制备了Ru-B/Al$_2$O$_3$·xH$_2$O和Ru-B/γ-Al$_2$O$_3$苯选择加氢制环己烯催化剂, 发现前者的性能更好. X射线衍射(XRD)和TEM结果表明, Ru-B/Al$_2$O$_3$·xH$_2$O具有更小的活性组分微晶和更高的分散度, 因而活性中心更多, 表观活性更高. 热分析(TG/DTA)结果表明, Ru-B/Al$_2$O$_3$·xH$_2$O具有结构H$_2$O, 所得的环己烯收率更高. Ning等[44,45]分别采用微乳液法-正硅酸乙酯原位水解形成载体、微乳液法-商品SiO$_2$载体以及普通的浸渍-化学还原法载体制备了RuC1, RuS1和RuS2三种催化剂. 结果表明, RuCl的活性和环己烯选择性均较高. XRD和TEM结果表明, RuC1和RuS1的活性比RuS2高是由于微乳液法制备的催化剂上金属Ru的粒径小, 具有较大的比表面积, 能暴露的活性位较多. RuC1上环己烯选择性比RuS1和RuS2上的高, 可能与RuC1催化剂表面较多的羟基和较高锌物种浓度以及较好的亲水性有关. 本课题组制备了Ru-M-B/ZrO$_2$, 发现在还原之前加入ZrO$_2$制得催化剂的选择性最高, 最佳Ru/ZrO$_2$比为0.13~0.16: 低于0.13时催化剂活性和选择性都较低; 高于0.16时, 催化剂活性较高, 但选择性较低[29,46]. 在催化剂中加入一定量的ZrO$_2$, 可以增加活性组分Ru的分散度, 使苯和Ru能够充分接触, 从而提高苯转化率. 此外, 亲水性ZrO$_2$的存在使催化剂表面形成一滞水层, 有利于环己烯脱附, 阻止环己烯继续加氢, 从而提高环己烯选择性. 我们还考察了ZrO$_2$焙烧温度对Ru-Fe-B/ZrO$_2$催化性能的影响, 发现随着载体焙烧温度升高, 催化剂活性降低, 环己烯选择性升高[47]. 结果表明, 催化剂活性降低与载体比表面积减小有关, 而选择性升高不但与载体比表面积, 而且还与载体的孔径增大和富含羟基的单斜相增加有关. 这与文献[48]结果一致. 综上可见, 亲水强、比表面积适中、孔结构简单和孔径较大的载体适宜作苯选择加氢制环己烯催化剂载体.

表2　助剂对非晶态合金催化剂性能的影响

Table 2　Effects of some promoters on the performance of amorphous alloy catalysts for benzene hydrogenation to cyclohexene

Sample	Time (min)	X_{BZ}/%	S_{HE}/%	Ref.
Ru-La-B/ZrO$_2$	30	58.7	75.1	[38]
Ru-Fe-B/ZrO$_2$	25	54.8	80.4	[30]
Ru-Zn-B	5	29.9	72.1	[41]
Ru-Zn-B/Zr(OH)$_4$·H$_2$O	55	73.1	62.3	[22]
Ru-Co-B/support	20	76.3	68.3	[49]
Ru-Zn-B/ZrO$_2$	15	58.2	81.8	[46]

3　反应条件的影响

3.1　温度的影响

研究表明, 随温度升高环己烯选择性先升高后降低. Ning等[44,45]根据物料的溶解度和分子运动论, 文献[49,50]则根据焓变和Arrhenius公式分别对这一现象进行了合理的解释. XRD结果表明, 加氢后催化剂的衍射峰变得尖锐, 晶粒变大; 且反应温

度越高, Ru 晶粒越大 (145, 153 和 179 °C 下, 反应后 Ru 的晶粒分别为 4.49, 5.08 和 5.59 nm)[50]. 同时, 在加氢后催化剂上还出现明显的 $NaBO_3$ 衍射峰, 说明在加氢过程中非晶合金逐渐分解[46]. 这可能也是导致反应温度超过 140 °C 后环己烯选择性降低的主要原因.

3.2 H_2 压的影响

Ning 等[44,45]考察了反应压力对 RuCl 催化剂性能的影响, 发现随着 H_2 压力的增大, 环己烯收率先升后降, 最佳压力为 6 MPa. 他们将此归结为两个原因. (1) 反应压力的改变可使苯加氢的机理发生改变. 当苯与氢摩尔比低时, 连续加氢机理起主要作用, 但在苯分压较高时, 一步加氢机理将起主要作用. 在 H_2 压力较低的情况下, 增大 H_2 压力, 苯在 Ru 催化剂上的分压下降. 因而有利于苯通过连续加氢机理进行反应, 反应过程中生成环己烯的几率大大提高, 环己烯选择性升高. 然而, 环己烯加氢生成环己烷的速率随着催化剂表面大量且过量吸附 H_2 的出现而加快, 故环己烯选择性随着压力的继续升高而降低. (2) 在苯加氢过程中, 各物质 (如苯和环己烯), 与 H_2 压力是不同的函数. 催化剂对生成环己烯反应而言存在一个理想的苯与 H_2 的覆盖度. 当催化剂表面存在大量且过量的吸附 H_2 时, 环己烯易加氢生成环己烷. 吴敏等[49]在负载型 Ru-Co-B 催化剂上发现了同样的现象. 本课题组也发现, Ru-M-B/ZrO_2 催化剂上最佳 H_2 压为 4~5 MPa [50].

3.3 搅拌速率的影响

传质在整个苯加氢反应过程中对环己烯选择性和收率起着主导作用. 当反应达到稳态时, 催化剂表面形成一滞水层, H_2、苯和环己烯在催化剂表面形成了一定的浓度梯度. 在该四相反应中, 提高搅拌速率可使催化剂颗粒在反应体系分布更加均匀; 同时有利于有机相以小的液滴分散在水相中, 增加气体、固体和液体接触面积, 加速传质过程, 使反应生成的环己烯分子立即从催化剂脱附, 避免进一步加氢生成环己烷. Ning 等[44,45]报道, 当搅拌速率由 400 r/min 增加到 800 r/min 时, 环己烯选择性升高; 但当搅拌速率大于 800 r/min 时, 继续加快搅拌速率对环己烯选择性的影响不大. 刘寿长等[50]发现, 对 Ru-M-B/ZrO_2 催化剂, 转速大于 900 r/min 时外扩散消除. 而对于 Ru-Co-B/载体催化剂, 吴敏等[49]发现消除外扩散时, 转速应大于 700 r/min[49]. 可见, 对于不同的催化剂, 适宜的搅拌速率不尽相同. 文献[49]还发现, 当搅拌速率大于 900 r/min, 催化剂出现粘壁现象, 导致反应速率下降. 因此, 搅拌速率也不能过快.

3.4 添加剂的影响

向反应浆液中添加无机或有机添加剂是提高环己烯选择性的重要途径之一. 其中以无机添加剂 (尤其是 $ZnSO_4$) 的作用最明显. 目前, 普遍认为 $ZnSO_4$ 作用有: (1) Zn^{2+}在催化剂表面的吸附, 增加了其亲水性, 有利于提高环己烯选择性[19,51]; (2) 反应浆液中的 $ZnSO_4$ 通过一种物理-化学力促进环己烯脱附[51]; (3) $ZnSO_4\cdot 7H_2O$ 的加入量影响反应浆液的 pH 和 B 物种的存在形式, 从而影响催化剂的活性和选择性[51]. 本课题组考察了 Zn^{2+}浓度和 pH 值对 Ru-Fe-B/ZrO_2 催化剂性能的影响[52]. 结果表明, Zn^{2+}浓度在 0.5~0.6 mol/L, 对应的 pH 为 5.4~5.5, 催化剂表现出较高的活性和环己烯选择性 (见表 3). 然而, 有关催化剂与 $ZnSO_4\cdot 7H_2O$ 相互作用的详细研究尚未见文献报道.

表 3 Zn^{2+}浓度对 Ru-Fe-B/ZrO_2 催化剂催化性能的影响

Table 3 Effects of Zn^{2+} concentrations on catalytic performance of Ru-Fe-B/ZrO_2 for benzene hydrogenation to cyclohexene

$[Zn^{2+}]$/(mol/L)	pH	X_{BZ}/%	S_{HE}/%	Y_{HE}/%
0	7.2	50.9	35.2	17.9
0.10	6.1	25.0	71.9	18.0
0.30	5.8	26.1	76.7	20.0
0.50	5.5	37.6	74.0	27.8
0.60	5.4	39.9	70.6	28.2
0.80	5.2	44.6	62.3	27.8

Reaction conditions: H_2O 280 ml, benzene 140 ml, Ru-Fe-B/ZrO_2 catalyst (Ru 0.64 g) 4 g, 140 °C, 5 MPa, stirring rate 1000 r/min, 5 min.

添加有机添加剂也是提高环己烯选择性的重要手段. Fan 等[53]制备了 Ru-Co-B/γ-Al_2O_3, 并研究了有机添加剂对该催化剂性能的影响, 结果列于表 4. 由表可见, 由于二乙醇胺水溶液为碱性, 能导致 $ZnSO_4$ 水解生成 $Zn(OH)_2$, 后者与二乙醇胺共同作用导致了环己烯选择性升高. 他们认为, 有机添加剂能提高环己烯选择性的原因为: (1) 吸附在催化剂表面的有机胺或醇能够与环己烯分子形成氢键, 这可减弱环己烯 C=C 键与 Ru 的 *d* 轨道的重叠程度, 使环己烯分子很快从 Ru 表面脱附, 因而环己烯

表 4 有机添加剂对 Ru-Co-B/γ-Al_2O_3 上苯选择加氢性能的影响

Table 4 Effect of organic additives on benzene hydrogenation over Ru-Co-B/γ-Al_2O_3 catalyst[53]

Additive	X_{BZ}/%	S_{HE}/%	Y_{HE}/%
None[a]	51.9	39.2	20.4
Ethanolamine	45.9	66.9	30.7
Diethanolamine	46.8	68.8	32.2
Glycine	49.4	37.5	18.5
β-Alanine	19.1	63.9	12.2
Diphenylamine	59.2	45.2	26.7
Triethylamine	52.8	44.4	23.4
Ethylenediamine	72.6	48.0	34.8
Diethylamine	44.2	62.3	27.5
1,3-Propanediol	66.3	45.4	30.1
Ethylene glycol	60.9	43.1	26.3
Glycerol	51.5	47.2	24.3
PEG-6000	79.3	43.4	34.4
PEG-400	72.2	31.5	22.8

Reaction conditions: benzene 3.00 ml, H_2O 4.0 ml, $ZnSO_4$ 0.70 mmol, additives 0.2 mmol, 150 °C, $p(H_2)$ = 5.0 MPa, stirring rate 1500 r/min, 1 h ([a]0.5 h).

选择性升高; (2) 这些有机物可提高 Zn 与 Ru 的相互作用; (3) 金属 Ru 与有机添加剂相互作用, 在催化剂表面可形成水层, 使得催化剂亲水性增加, 环己烯选择性升高; (4) 有机添加剂 N 或 O 上的电子向 Ru 转移, 使 Ru 富电子, 减弱了 Ru 对环己烯的吸附能力, 因此环己烯易从催化剂表面脱附, 环己烯选择性升高.

虽然无机添加剂 (尤其是 $ZnSO_4$) 的添加获得了很高的环己烯收率, 并已经应用于工业生产, 但 $ZnSO_4$ 溶液为酸性, 在高温下具有腐蚀性, 加氢需要在耐酸的哈氏合金釜中进行. 此外, $ZnSO_4$ 还能导致催化剂迅速失活. 开发无添加剂催化体系成了苯选择加氢制环己烯的一个重要研究方向. Fan 等[36]制备了 Ru-Co-B/γ-Al_2O_3 催化剂, 在无添加剂和最优的条件下, 环己烯收率可达 28.8%, 并且循环使用 6 次, 催化剂活性和选择性几乎不变, 可见催化剂有较高的稳定性 (见图 3).

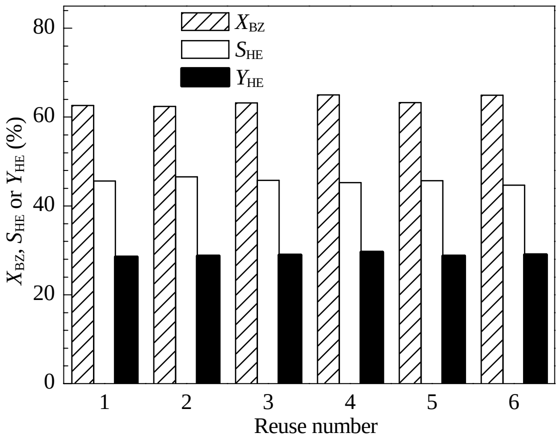

图 3 3.8%Ru-1.2%Co-B/γ-Al_2O_3 催化剂的重复使用性能

Fig. 3. Reusability of 3.8%Ru-1.2%Co-B/γ-Al_2O_3 catalyst.[36] Reaction conditions: catalyst 40 mg, H_2O 4.0 ml, 140 °C, $p(H_2)$ = 5.0 MPa.

3.5 预处理的影响

预处理是将催化剂在反应浆液 ($ZnSO_4$ 溶液) 中于反应条件下保持 1 h 或更长的时间, 工业运行为 22 h[54]. 本课题组研究了预处理对 Ru-Fe-B/ZrO_2 催化剂性能的影响, 发现预处理后催化剂的活性明显下降, 环己烯选择性显著升高. 为减轻后处理工艺压力, 工业要求 $\gamma_{40} > 100$, $S_{HE}(40) > 80\%$[50]. 其中, γ_{40} 为催化剂的活性指数, 表示每克催化剂每小时转化苯的克数; $S_{HE}(40)$ 为苯转化 40% 时, 环己烯的选择性. 经过预处理后, Ru-Fe-B/ZrO_2 催化剂的 γ_{40} = 351.6, $S_{HE}(40)$ = 83.33%, 完全达到要求. 我们认为, 预处理的作用有: (1) 预处理后, H_2 优先吸附在强活性中心上, 苯吸附在中等强度的活性中心上, 此时苯既可被活化, 中间产物环己烯又容易脱附[50]; (2) 使催化剂钝化和结构稳定化, 延长催化剂使用寿命[55]; (3) 使催化剂孔径向大孔分布移动, 有利于环己烯的溢出, 因而环己烯选择性提高[55].

4 催化剂活性和选择性的调变性研究

催化剂活性和选择性的可调变性是指向反应浆液中添加酸性或碱性物质, 以调变催化剂活性和选择性, 在不改变催化剂量的前提下, 弥补催化剂随时间的延长, 反应条件波动或其它因素的影响而引起的活性和选择性对正常值的偏离, 从而维持催化剂的正常运转[30,56].

本课题组考察了 ZnO 和 H_2SO_4 用量及其加入方式对该催化剂性能的影响, 研究了 Ru-Fe-B/ZrO_2 催化剂活性和选择性的可逆调变性, 并推测了反应机理[35]. 结果表明, 随着 ZnO 用量的增加, 苯转化率降低, 环己烯选择性升高; 随着 H_2SO_4 用量的增加, 苯转化率升高, 环己烯选择性降低. ZnO 和 H_2SO_4 的加入方式对催化剂性能的影响程度不同. 且 ZnO 和 H_2SO_4 可以可逆调变催化剂的活性和选

择性. 我们认为, 它们可以可逆地改变化学吸附在催化剂表面的 Zn 含量, 进而改变 Ru 活性中心的分布、形态和电子密度, 这是 Ru-Fe-B/ZrO_2 催化剂活性和选择性可以可逆调变的原因. 化学吸附的特点是造成两种加入方式对催化性能影响差异的主要原因, 同时这也是调变过程中催化剂活性和选择性与空白实验不同的原因.

5 催化剂中试结果

5.1 间歇式结果

2002 年, 在国家科技部科技型中小企业创新基金的资助下, 我们课题组与企业联合, 完成了催化剂的中试放大生产, 并在 50 L 间歇式反应釜上完成了催化剂工艺的中试[52]. 结果表明, 当 Zn^{2+}浓度由 0.5 mol/L 增加到 0.6 mol /L 时, Ru-Fe-B/ZrO_2 的催化活性和选择性均升高; 当 Zn^{2+}浓度为 0.5 mol/L 时, 向反应浆液添加分散剂 ZrO_2 催化剂的活性和环己烯选择性均升高. 分散剂的最佳量为 $m(\mathrm{Cat})/m(\mathrm{ZrO_2}) = 1/2$; 超过这个用量后, 催化剂活性略有升高, 但环己烯选择性大幅度降低. 在 130~135 °C, 4.5~5.0 MPa, 水苯比为 2:1, Zn^{2+}浓度为 0.5 mol/L, $m(\mathrm{Cat})/m(\mathrm{ZrO_2}) = 1/2$ 和预处理 12 h 等最佳工艺条件下, 苯转化率 40% 时, 环己烯选择性为 80%, 接近实验室水平.

5.2 连续式结果

本课题组与企业联合, 在 100 L 不锈钢连续装置 (见图 4) 上, 考察了催化剂活性、选择性、可调变性、再生和寿命等重要指标[37,38,55].

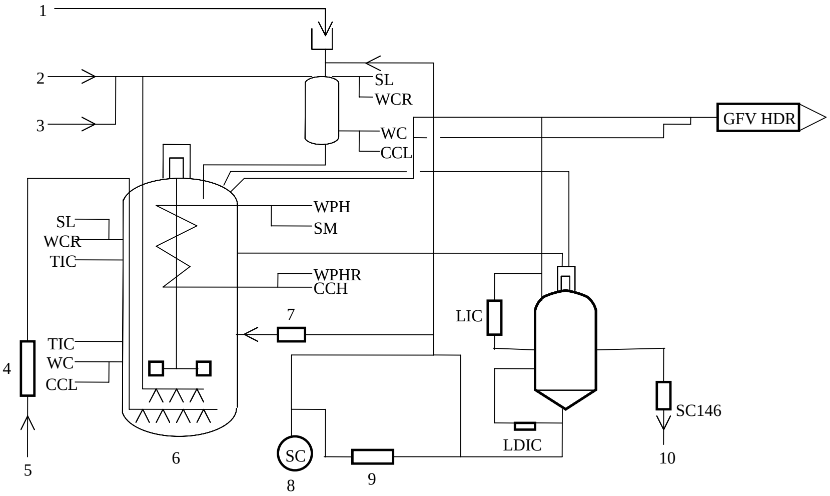

图 4 连续式中试装置流程图

Fig. 4. Diagram of a consecutive pilot plant [37]. 1—Catalyst inlet; 2—Hydrogen inlet; 3—Nitrogen inlet; 4—Benzene flow meter; 5—Benzene inlet; 6—Discharge opening; 7—Slurry flow meter; 8—Opening for catalyst; 9—Slurry circulation pump; 10—Opening for product. SL—Low-pressure steam; WCR—Returning cooling water; WC—Cooling water; CCL—Low-pressure circumfluent condensate; WPH—High pure water; SM—Medium-pressure steam; WPHR—Returning high pure water; CCH—High-pressure circumfluent condensate; TIC—Temperature indicating controlling; SC—Solenoid-controlled valve; LIC—Level indicating controlling; LDIC—Level difference indicating controlling; SC146—Solenoid-controlled valve 146; GFV HDR—General fuel gas vent header.

图 5 为 Ru-La-B/ ZrO_2 (郑大) 催化剂与 Ru-Zn (进口) 催化剂的活性和选择性. 可以看出, 100 h 之前, 郑大催化剂的活性远远高于进口催化剂. 反应 100~170 h 时, 二者活性接近. 郑大催化剂的选择性随时间延长而逐步稳定地升高; 40 h 之后, 郑大催化剂的选择性明显高于进口催化剂. 另外, Ru-La-B/ZrO_2 中有效 Ru 含量 (0.18 kg) 仅为 Ru-Zn (0.45 kg) 的 40%.

在连续装置上, 我们还详细研究了催化剂的再生[38,55]. TEM 结果表明, 催化剂团聚和非晶态晶化是催化剂失活的重要原因. 反应前后浆液和催化剂中的 Fe^{2+}和 Zn^{2+}检测结果表明, 催化剂失活主要是由于长期运转过程中吸附了反应浆液中的 Zn^{2+}以及由器壁引入的 Fe^{2+}造成的, 据此确定了酸洗再生方法. 表 5 为失活催化剂再生前后的活性和选择性数据. 结果表明, 酸洗后, 催化剂的活性和选择性基本可以恢复. 根据对洗涤液中 Zn^{2+}和 Fe^{2+}的含量分析, HCl (2.0 mol/L) 能洗去更多的 Fe^{2+}和全部的 Zn^{2+},

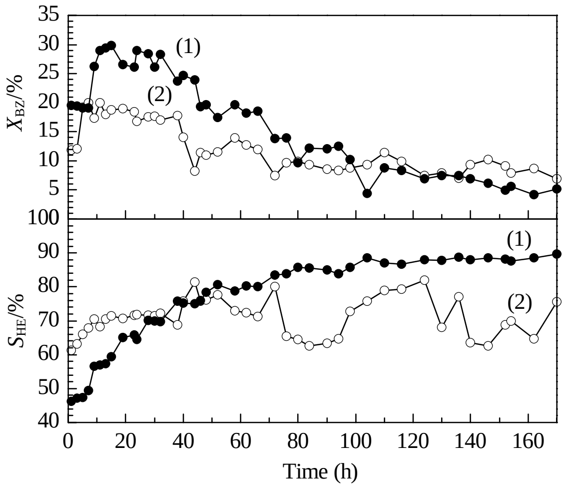

图 5 中试装置上两种催化剂的性能

Fig. 5. Catalytic performance of two catalysts for benzene hydrogenation to cyclohexene in the pilot plant [55]. (1) Ru-La-B/ZrO_2; (2) Ru-Zn. Run conditions: catalyst 1.35 kg, H_2O 170 ml, ZrO_2 1.35 kg, $ZnSO_4·7H_2O$ 17 kg, $p(H_2)$ = 4.4–4.5 MPa, 135 °C, stirring rate 900 r/min, pretreated for 10–22 h, circulation velocity of the slurry 130–150 kg/h, circulation velocity of benzene 13–150 kg/h.

催化剂再生后效果也最好.

图 6 为在中试装置上补加再生催化剂后和 340~466 h 的活性和选择性. 可以看出, 补加再生催化剂后, 苯转化率最高上升至 30.6%, 维持高于 24.0% 的时间为 14 h. 环己烯选择性虽有所降低, 但随着时间的延长而略有升高. 还可以看出, 通过再生和调变, 466 h 内苯转化率一直在 20% 以上, 环己烯选择性维持在 55% 以上. 这表明通过中试我们已经建立了一套完整的用非晶态催化剂催化苯选择加氢制环己烯催化体系.

表 5 洗涤前后催化剂的活性和选择性

Table 5 Activity and selectivity of Ru-La-B/ZrO_2 catalyst before and after washing[38]

Condition	X_{BZ}/%			S_{HE}/%		
	5 min	10 min	15 min	5 min	10 min	15 min
Before washing	6.5	11.4	16.5	60.4	50.2	31.4
After washing with H_2O	6.1	9.5	13.4	65.4	61.5	48.5
After washing with 0.5 mol/L HCl	10.8	18.8	27.6	65.8	61.2	49.6
After washing with 2.0 mol/L HCl	14.5	23.2	32.5	59.6	57.8	51.4
After washing with 1.0 mol/L H_2SO_4	11.6	20.2	29.3	68.0	57.0	48.9

Run conditions: H_2O 58 ml, benzene 29 ml, catalyst 0.45 g, $ZnSO_4$ 7.2 g, 150 °C, $p(H_2)$ = 5.0 MPa, stirring rate 900 r/min.

6 结论与展望

在苯选择加氢反应中, Ru-M-B/ZrO_2 不但具有较高的活性和选择性, 而且具有 Ru 活性组分利用率高和制备方法简捷等优点. 这是工业化沉淀法制备 Ru-Zn 催化剂所无法比拟的, 因而成为目前苯选择加氢制环己烯的 Ru 基催化剂中最具竞争力的方法. 但是, 目前连续式中试装置催化剂的性能与间歇式中试装置催化剂仍有一定差异, 没有取得理想的效果. 因此, 今后的主要任务是研究间歇工艺和连续工艺之间的差别, 改善工艺条件, 提高催化剂性能, 使 Ru 基非晶态合金催化剂获得工业应用. 此外, 利用非晶态合金催化剂在无添加剂条件下催化苯选择加氢, 虽然现在环己烯收率仅有 28.8%, 且环己烯选择性较低, 但该工艺具有催化剂稳定性高、对

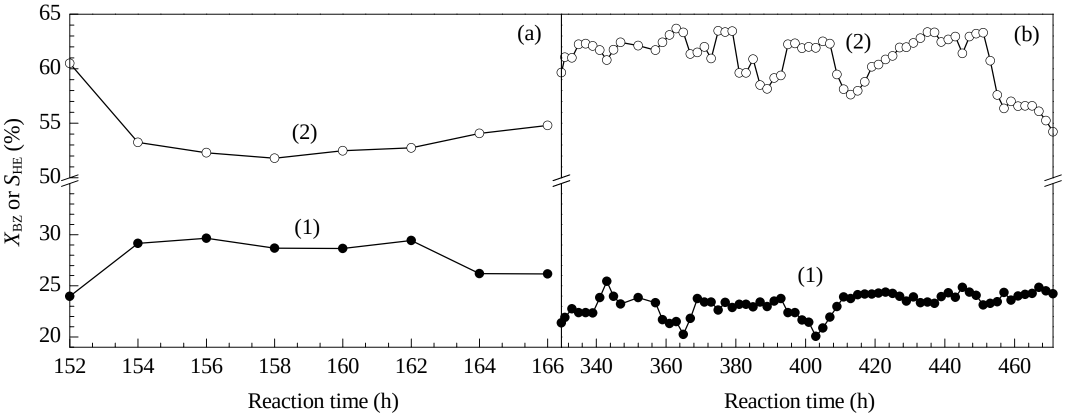

图 6 中试装置上加入再生 **Ru-La-B/ZrO_2** 催化剂后和 **330~470 h** 的活性和选择性

Fig. 6. Activity and selectivity after adding the regenerated Ru-La-B/ZrO_2 catalysts (a) and during 330–470 h (b).[38] (1) *X*(BZ); (2) *S*(HE). Run conditions: catalyst 1.35 kg, H_2O 170 ml, ZrO_2 1.35 kg, $ZnSO_4·7H_2O$ 17 kg, $p(H_2)$ = 4.4–4.5 MPa, 135 °C, stirring rate 900 r/min, pretreated for 10–22 h, circulation velocity of the slurry 130–150 kg/h, circulation velocity of benzene 13–150 kg/h.

反应器要求较低和操作简易等突出优点, 势必也将成为今后研究的一个重要方向.

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英译文
English Text

The production of nylon 6 and nylon 66 from benzene and cyclohexene has attracted much attention because this is a safe and environmentally benign process with atomic economy, and is preferred to the route from benzene and cyclohexane [1–9]. In 1989, Asahi Chemical Company industrialized the process for the selective hydrogenation of benzene to cyclohexene using an unsupported Ru-Zn catalyst that had high activity and excellent cyclohexene selectivity [10]. However, the catalytic efficiency in terms of the utilization per unit mass of Ru was low, the catalyst had poor resistance to S, Cl, and Fe, and was costly [11]. Furthermore, the preparation technology of the catalyst has not been licensed so far. Since the 1990s, Chinese universities and research institutes have studied this reaction and developed novel catalysts and catalytic technologies [12–16]. The research results with supported amorphous alloys have been most remarkable for their high activity and excellent selectivity due to their short range ordering and long range disordered structure and high concentration of coordinatively unsaturated sites [17]. Thus amorphous alloy nano-particles have received increasing attention as novel catalytic materials since 1981 [18]. In 1999, Xie et al. [19] reported that a Ru-B amorphous alloy catalyst prepared by a chemical reduction method gave a cyclohexene yield from the selective hydrogenation of benzene of 31.2%. This led to Ru-based amorphous alloy catalysts becoming the focus of the research on novel catalytic materials for the selective hydrogenation of benzene to cyclohexene. Zhengzhou University [20,21], Fudan University [22], Dalian Institute of Chemical Physics [23], and Sinopec Corp. Research Institute of Petroleum Processing [24] have received patents for the preparation methods of amorphous alloy catalysts for the selective hydrogenation of benzene to cyclohexene. Progress in amorphous alloy catalysts for the selective hydrogenation of benzene to cyclohexene is reviewed in this article, with the emphasis on the research results of Zhengzhou University.

1 Thermodynamics and kinetics of selective hydrogenation of benzene to cyclohexene

The thermodynamics indicate it would be difficult to get cyclohexene from benzene 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. The mechanism for benzene hydrogenation proposed by Prasad et al. [25] has been generally accepted. The main features of it are the simultaneous presence of two reaction routes. Route 1 is consecutive hydrogenation, in which benzene is successively hydrogenated to cyclohexane from cyclohexadiene and cyclohexene. Route 2 is one step hydrogenation of benzene to cyclohexane. Therefore, in order to improve the yield of cyclohexene, it is necessary to stop the further hydrogenation of cyclohexene and inhibit the complete hydrogenation of benzene. Hydrophilic modification of the Ru-based catalyst is one of the most effective ways to achieve this effect. This was first proposed by Struijk et al. [5,6] and has been confirmed by the observation that the cyclohexene yield is closely related to the hydrophilicity of support [26,27]. It was further proved by the solubility of benzene and cyclohexene in water. The solubility of benzene in water is 125 mol/m^3, which is 6 times that of cyclohexene (21 mol/m^3). Thus the stagnant water layer on the catalyst surface would increase the concentration of benzene, which promotes desorption of cyclohexene from the catalyst surface by competitive adsorption. In addition, the stagnant water layer can effectively prevent the further hydrogenation of cyclohexene to cyclohexane because of the low solubility of cyclohexene in water. This is depicted in Fig. 1. This hydrophilic modification is now an important guiding principle for the development of catalysts for the selective hydrogenation of benzene to cyclohexene.

The kinetic equations for the selective hydrogenation of benzene to cyclohexene over a Ru-Zn-B/ZrO_2 catalyst have been established by our group [28] for the case where the one step hydrogenation of benzene to cyclohexane can be neglected (because a tri-molecular reaction is very rare).

Low pressure：

$$\frac{\mathrm{d}c(\mathrm{HE})}{\mathrm{d}t}=-\frac{\mathrm{d}c(\mathrm{BZ})}{\mathrm{d}t}+\frac{\mathrm{d}c(\mathrm{HE})}{\mathrm{d}t}=k_1c(\mathrm{BZ})p^2(\mathrm{H_2})-k_2p^2(\mathrm{H_2}) \quad (1)$$

Medium pressure：

$$\frac{\mathrm{d}c(\mathrm{HE})}{\mathrm{d}t}=-\frac{\mathrm{d}c(\mathrm{BZ})}{\mathrm{d}t}+\frac{\mathrm{d}c(\mathrm{HE})}{\mathrm{d}t}=\frac{k_1c(\mathrm{BZ})\sigma p^2(\mathrm{H_2})}{1+\sigma p^2(\mathrm{H_2})}-\frac{k_2\sigma p^2(\mathrm{H_2})}{1+\sigma p^2(\mathrm{H_2})} \quad (2)$$

High pressure：

$$\frac{\mathrm{d}c(\mathrm{HE})}{\mathrm{d}t}=-\frac{\mathrm{d}c(\mathrm{BZ})}{\mathrm{d}t}+\frac{\mathrm{d}c(\mathrm{HE})}{\mathrm{d}t}=k_1c(\mathrm{BZ})-k_2 \quad (3)$$

The concentrations in the reaction calculated by the integration of the simplified differential equations above were approximately in agreement with experimental values. The reaction order for cyclohexene was zero, and the reaction orders for hydrogen at low, middle, high pressure were two, fractional, and zero, respectively. This implied that the catalyst surface rapidly adsorbed cyclohexene and was saturated by it. However, the adsorption of hydrogen was related to the pressure of hydrogen and the surface can reach saturated adsorption of hydrogen only at a high enough pressure of hydrogen. Hence, the selective hydrogenation of benzene is generally carried out at a H_2 pressure of 5.0 MPa. As can be seen from Eq. (3), the increase in k_1 and the decrease in k_2 would enhance the selectivity for cyclohexene. It was found that a hydrophilic catalyst or the addition of a substance that enhanced the hydrophilicity of the catalyst would increase k_1 and decrease k_2.

2 Structure and formation of a Ru-based amorphous alloy catalyst

2.1 Amorphous structure and crystallite size effects

Xie et al. [19] reported that the activity and cyclohexene selectivity over an amorphous Ru-B/SiO_2 catalyst were both higher than those over a crystalline Ru-B/SiO_2 catalyst due to the structural effect of the amorphous alloy. Our group [29,30] have prepared Ru-M-B/ZrO_2 (M = Zn, Co, and Fe) nano-amorphous alloy catalysts. The Ru crystalline sizes of these catalysts were in range of 3.6–5.3 nm. The transmission electron microscopy (TEM) and selected area electron diffraction (SAED) images are shown in Fig. 2. The cyclohexene selectivity reached 80.0% at a benzene conversion of 54.8% at 25 min over the Ru-Fe-B/ZrO_2 catalyst. We proposed that the special properties of the catalysts were derived from the combination of the nano-scale size of the particles and the amorphous materials, which gave high activity and excellent selectivity. Bu et al. [8] reported that the highest cyclohexene yield was obtained over the Ru-Ba/SBA-15 catalyst with a Ru crystalline size of 5.6 nm, and suggested that this crystallite size of Ru had the highest amount of the active sites favorable for the production of cyclohexene. Nagahara et al. [10] reported that the Ru crystalline size of Asahi’s Ru-Zn catalyst was also about 5 nm. These results indicate that the amorphous structure and crystallite size effects play a key role in the catalysts for the selective hydrogenation of benzene.

2.2 Boron effects

Xie et al. [19] prepared a supported Ru-B/SiO_2 catalyst by impregnation and chemical reduction. The benzene conversion over this catalyst was 3.2%/(g·h) and the cyclohexene selectivity was 49.7%, which were much better than the activity (2.3%/(g·h)) and selectivity (22.2%) over a Ru/SiO_2 catalyst with the same Ru loading obtained by H_2 reduction. X-ray photoelectron spectroscopy (XPS) and Ar^+ etching results suggested that the B in the Ru-B/SiO_2 catalyst existed in the two forms of the elemental and oxidative states, and was enriched on the catalyst surface. Some electrons were transferred from elemental B to metallic Ru, making Ru electron rich. They suggested that the hydrophilic modification of the catalyst by B was one of the most important factors responsible for the high activity and excellent cyclohexene selectivity. On the one hand, oxidative states of boron species dispersed on the catalyst surface can bond water molecules through hydrogen bonding. On the other hand, electron transfer from elemental B to Ru made the elemental B electron deficient and the electron deficient B can more easily accept the lone electron pair on the oxygen of water. Therefore, the hydrophilicity of the catalyst was enhanced and the selectivity for cyclohexene was increased. Liu et al. [31] prepared a series of Ru-B catalysts with different B contents by chemical reduction, and found that with the increase of the B content from 0 to 10.1%, cyclohexene yield increased from 6.3% to 30.4% and cyclohexene selectivity increased from 19.4% to 50.8%. This is shown in Table 1. It indicated that by varying the B content in Ru-B amorphous alloys, the activity and cyclohexene selectivity can be significantly enhanced. Besides the reduction temperature, the pH value during the dropwise addition of $NaBH_4$ [32], the concentration and addition rate of $NaBH_4$ [30,33–35] also can modify the B content in the amorphous alloy catalyst. Therefore, these conditions should be specially noted during the preparation of the amorphous alloy catalysts.

2.3 Promoter effects

It was reported that some promoters such as Fe, Zn, La, Ce, and Co at some loadings can increase the cyclohexene selectivity and decrease the activity, and other promoters can increase both cyclohexene selectivity and the activity. The effects of these can be slightly different with different preparation methods [36–42]. Generally, the roles of promoters are attributed to the electronic and structural effects. Fan et al. [36] prepared a Ru-Co-B/γ-Al_2O_3 catalyst and found that the Co in the catalyst was in an oxidized state and there was partial electron transfer from Ru to Co. The formation of $Ru^{\delta+}$ gave a much smaller reduction peak of Ru(III), which was confirmed by XPS and temperature-programmed reduction (TPR). Thus they suggested the presence of $Ru^{\delta+}$ improved cyclohexene selectivity since cyclohexene was weakly adsorbed and easily desorbed from $Ru^{\delta+}$ species. Our group has reported XPS data [37,38] that showed that La also existed in an oxidized state and there was partial electron transfer from La to Ru. Moreover, La in the oxidized state can be reduced to the metal with a long reaction time. We also found that most of the promoters that improve cyclohexene selectivity were transitional metals. Although these metals showed no catalytic activity for hydrogenation, they had vacant *d*-orbitals that can interact with the π-electrons of cyclohexene and pull cyclohexene away from Ru. This would result in the immediate desorption of cyclohexene once it was formed [39–41]. All these supported the existence of an electronic interaction between the promoter and Ru that affected the activity and selectivity of the catalyst. Some promoters also act as structural modifiers. The roles of a structural promoter are attributed to the following: (1) increase the dispersion of the active component and depress the agglomeration of the Ru active component [36]; (2) block the active sites on which the hydrogenation of cyclohexene occurs rapidly and provide an unsuitable environment for the hydrogenation of cyclohexene [36,40]; (3) improve the stability of the Ru-B/ZrO_2 amorphous alloy catalyst and delay the crystallization of the amorphous alloy [42]; (4) make the Ru-B active component disperse well and provide a homogenous coordination environment for the active component [42].

It is found that the precursor of the promoter, distribution of the promoter, and residual NaOH formed during the reduction also have large effects on the performance of the catalyst. Our group [43] introduced Cu into the Ru-Fe-B/ZrO_2 catalyst and prepared a catalyst with two promoters. We found that the activity of the Ru-Fe-Cu-B/ZrO_2 catalyst did not decrease when compared with the Ru-Fe-B/ZrO_2 catalyst, but the selectivity of the former increased slightly. We also showed that the use of $CuCl_2·2H_2O$ as the precursor had a better effect on the enhancement of the activity and cyclohexene selectivity than $CuSO_4·5H_2O$. We proposed that on the one hand Cl^- preferentially adsorbed on the active sites and the adsorption of cyclohexene on the remaining active sites was weak. This favored the desorption of cyclohexene and increased cyclohexene selectivity. On the other hand, Cl^- adsorbed on the catalyst surface can bond water molecules through hydrogen bonding. This enhanced the hydrophilicity of the catalyst and improved cyclohexene selectivity. However, SO_4^{2-} had no such functions. Qin et al [41] prepared an unsupported Ru-Zn-B catalyst and found that the feed method affected the distribution of the Zn content on the catalyst. They suggested that in the use of the inverse addition method (the mixed solution of $RuCl_3$ and $ZnSO_4$ was dropped into the solution of $NaBH_4$), the amount of $NaBH_4$ was much more than that needed for the reduction of Ru^{3+} and Zn^{2+} throughout the reduction process, which ensured the simultaneous reduction of Ru^{3+} and Zn^{2+}. Thus the distributions of the Ru and Zn contents were uniform, which was responsible for the high activity and excellent cyclcohexene selectivity of catalysts prepared by this method. However, in the direct addition method (the solution of $NaBH_4$ was added to the mixed solution of $RuCl_3$ and $ZnSO_4$), Ru^{3+} was preferentially reduced and the Ru active sites were covered by the later reduced Zn, which led to the decrease in the activity. Qin et al. [41] and our group [30] also investigated the effect of residual of NaOH on the performance of catalyst. The results showed that the catalyst exhibited good performance when the pH value of the filtrate was 8 or 7.5, that is, a small amount of NaOH remained on the surface of the catalyst. We suggested that the alkali metal ions left acted as an electronic promoter. Meanwhile, the OH^- left both enhanced the hydrophilicity of the catalyst and also reacted easily with Zn^{2+} in the slurry to form a small amount of $Zn(OH)_2$, which were both favorable to the increase of cyclohexene selectivity. The effects of different promoters on the performance of amorphous alloy catalysts are shown in Table 2.

2.4 Support effects

Wang et al. [27] prepared a Ru-B/$Al_2O_3·xH_2O$ catalyst and a Ru-B/γ-Al_2O_3 catalyst by a combined coprecipitation-crystallization-reduction strategy and found that the activity and cyclohexene selectivity of the former were superior to the latter. X-ray diffraction (XRD) and TEM results showed that the former had a higher dispersion of much smaller RuB particles. Thus the former possessed more active sites and exhibited the higher activity. The thermal analysis (TG/DTA) results showed that the superior selectivity of the former was attributable to the existence of more structural water and surface hydroxyl groups on the former than those on the latter. Ning et al. [44,45] prepared three kinds of catalysts:

RuCl, RuS1, and RuS2 by microemulsion processing and the hydrolysis product of tetraethyl orthosilicate as the support, microemulsion processing and a commercial silica as the support, and the conventional impreparation-chemical reduction method, respectively. They found that the RuCl catalyst gave a higher activity and better cyclohexene selectivity. XRD and TEM results showed that RuC1and RuS1 showed a higher activity than RuS2 because of a smaller Ru particle size and more specific surface. There were more exposed active sites on the two former catalysts prepared by microemulsion processing. The superior cyclohexene selectivity over the RuC1 catalyst might be attributed to the much higher content of surface hydroxyl groups and zinc compounds, which resulted in a large enhancement of the hydrophilicity of the catalyst. Our group [29,46] prepared Ru-M-B/ZrO_2 catalysts, and found that the catalyst prepared with the addition of ZrO_2 before the reduction exhibited the best cyclohexene selectivity, and the optimal Ru/ZrO_2 ratio was in the range of 0.13 to 0.16. Below this range the activity and the cyclohexene selectivity were both very low. When the ratio was above 0.16, the activity of the catalyst was improved but the cyclohexene selectivity was decreased. With the addition of some amount of ZrO_2 as support, the dispersion of the active component of Ru was increased, which led to an adequate contact between Ru active sites and benzene and the enhancement of the activity of the catalyst. Moreover, the existence of hydrophilic ZrO_2 resulted in the formation of a stagnant water layer on the surface of the catalyst, which promoted desorption of cyclohexene, suppressed the further hydrogenation of cyclohexene, and enhanced cyclohexene selectivity. We also investigated the influence of the calcination temperature of ZrO_2 on the performance of a Ru-Fe-B/ZrO_2 catalyst, and found that the activity decreased and cyclohexene selectivity increased with increased calcination temperature [47]. We suggested that the decrease of the activity was related to the decrease of the support specific surface area, and the increase of the cyclohexene selectivity was due not only to the decrease of the support specific surface area but also to the increase in pore diameter and increase in the monoclinic ZrO_2 phase with a high surface hydroxyl content, in agreement with the conclusion in the literature [48]. This suggested that supports with strong hydrophilicity, medium specific surface area and large pores, and a simple pore structure were suitable for supporting the catalyst for the selective hydrogenation of benzene to cyclohexene.

3 Hydrogenation condition effects

3.1 Reaction temperature

It was reported that the cyclohexene selectivity first increased and then decreased with the increase of the temperature [44,45,49,50]. The literature [49,50] used the enthalpy change and Arrhenius equation and Ning et al. [44,45] used the solubility of the reactant and molecular kinetic theory to explain this. XRD results showed that the diffraction peaks of the catalyst after the hydrogenation were sharper, which indicated an increase of the crystallite size. A higher temperature gave a larger crystallite size. The Ru crystallite sizes of the catalyst after the hydrogenation were 4.49, 5.08, and 5.59 nm, respectively, at 145, 153, and 179 ^{o}C [50]. The obvious diffraction peaks of $NaBO_3$ observed in the XRD patterns of the catalyst after hydrogenation indicated the gradual decomposition of the amorphous alloy [46]. This may be one of the main reasons for the decrease of cyclohexene selectivity when the reaction temperature exceeded 140 ^{o}C.

3.2 Hydrogen pressure

Ning et al. [44,45] investigated the effect of hydrogen pressure on the performance of the RuCl catalyst and found that cyclohexene yield first increased and then decreased with increasing pressure, and the optimum pressure was 6 MPa. They suggested that this can be ascribed to the following two effects. (1) The routes of the hydrogenation of benzene were influenced by the hydrogen pressure. The consecutive hydrogenation mechanism dominated at low molar ratios of benzene to hydrogen, and the one step hydrogenation mechanism became more important at higher benzene pressure. Under a low hydrogen pressure, increasing hydrogen pressure would decrease benzene partial pressure at the surface of ruthenium. Thus, this benefited benzene hydrogenation by the consecutive mechanism, and the probability of the formation of cyclohexene was greatly increased and the cyclohexene selectivity was enhanced. However, the rate of cyclohexene hydrogenation to cyclohexane would also increase when there was an excessive amount of hydrogen on the surface. As a result, the selectivity for cyclohexene would decline with the further increase of the pressure. (2) The rates of hydrogenation of the reactant benzene and cyclohexene were different functions of the hydrogen pressure, and the hydrogenation rate of these would change with the hydrogen pressure. The rate of benzene to cyclohexene would increase gradually with an increase in hydrogen pressure to a maximum corresponding to the optimal surface coverage of benzene and hydrogen. However, at higher hydrogen pressure, a smaller portion of empty active sites available for benzene would give a lower hydrogenation rate for benzene. At the same time, cyclohexene was easily hydrogenated to cyclohexane when there was an excessive amount of hydrogen on the surface. Wu et al. [49] also observed this same phenomenon over a Ru-Co-B supported catalyst. Our group reported that the optimum hydrogen pressure was 4–5 MPa over the Ru-M-B/ZrO_2 catalyst [50].

3.3 Stirring rate

Mass transport plays a dominant role in the cyclohexene yield and selectivity in the reaction. When the reaction reaches a steady state, a stagnant water layer forms on the surface of the catalyst and a concentration gradient on the surface of the catalyst exists. In this multiphase reaction, increasing the stirring rate is beneficial for getting a better dispersion of the catalyst particles. Meanwhile, increasing the stirring rate is also favorable for better dispersion of smaller droplets of the organic phase in the water and enlarges the contact area between the gas, solid, and liquid. Thus mass transfer is accelerated, promoting desorption of cyclohexene and suppressing further hydrogenation of cyclohexene. Ning et al. [44,45] reported that cyclohexene selectivity increased when the stirring rate was increased from 400 to 800 r/min, but above 800 r/min the cyclohexene selectivity increase was not obvious. It was reported that external diffusion limitation can be eliminated at stirring rates above 900 r/min for the Ru-M-B/ZrO_2 catalyst [50], and above 700 r/min for the Ru-Co-B/support catalyst [49]. This indicated different stirring rates were needed to eliminate external diffusion limitation for different catalysts. In addition, Wu et al. [49] also found that particles of the catalyst adhered to the inner wall of the reactor when the stirring rate exceeded 900 r/min, which resulted in a decrease of the reaction rate. This suggested that the stirring rate should not be too high.

3.4 Additive

The addition of inorganic and organic additives is one of the most important methods for improving cyclohexene selectivity. Among these, the inorganic additives, especially $ZnSO_4$, gave the best effect. The roles of $ZnSO_4$ can be attributed to the following three reasons. (1) Adsorption of Zn^{2+} on the surface of the catalyst can improve the hydrophilicity of the catalyst surface, which is beneficial to improving cyclohexene selectivity [19,51]. (2) $ZnSO_4$ in the reaction slurry can promote desorption of cyclohexene through a physical-chemical interaction [51]. (3) The pH value of the reaction slurry change with the amount of $ZnSO_4{\cdot}7H_2O$, resulting in the existence of different forms of B. As a consequence, the activity and the cyclohexene selectivity of the catalyst were affected [51]. Our group [52] investigated the influences of different zinc ion concentration and pH value on the performance of the Ru-Fe-B/ZrO_2 catalyst, and found the optimal concentration of Zn^{2+} in the slurry was in range of 0.5–0.6 mol/L with the pH value of 5.4–5.5. The catalyst exhibited high activity and excellent cyclohexne selectivity, as shown in Table 3. However, detail studies on the interaction between the catalyst and $ZnSO_4$ have not yet been presented in the open literature.

Another important method for enhancing cyclohexene selectivity is by the addition of organic additives into the reaction slurry. Fan et al. [53] prepared a Ru-Co-B/γ-Al_2O_3 catalyst and investigated the effects of organic additives on the performance of this catalyst. The results are shown in Table 4. They found that diethanolamine caused the hydrolysis of $ZnSO_4$ to generate $Zn(OH)_2$ by the basicity of its aqueous solution, and the synergistic effect of $Zn(OH)_2$ and diethanolamine resulted in the enhancement of cyclohexene selectivity. They suggested that the roles of the organic additives on the improvement of cyclohexene selectivity were the following four. (1) Organic amines or alcohols adsorbed on the surface of the catalyst can bond with cyclohexene through hydrogen bonding. This significantly weakens the overlap of the π-electrons of the C=C double bond in cyclohexene with the *d* orbital of ruthenium and caused the hydrogen-bonded cyclohexene to desorb rapidly, resulting in the increase of cyclohexene selectivity. (2) Some organic additives improve the interaction between Zn species and metallic Ru. (3) Interaction between Ru active sites and the organic additives lead to the formation of a stagnant water layer on the surface of the catalyst, resulting in the increase of the hydrophilicity of the catalyst surface. (4) Electron transfer from N or O in the organic additives to the *d* orbital of ruthenium probably occurred and made ruthenium become electron-rich, resulting in the easy desorption of cyclohexene and the increase of cyclohexene selectivity.

Although the addition of inorganic additives, especially $ZnSO_4$, can achieve a high cyclohexene yield and had been successfully applied in industrial production, $ZnSO_4$ is a strongly corrosive medium due to the acidity of its hydrolysis, and thus the hydrogenation has to be performed in Hastelloy alloy units with a good acid resistance. In addition, $ZnSO_4$ can lead to a rapid deactivation of the catalyst. Therefore, the use of no additives for the benzene selective hydrogenation to cyclohexene is becoming a new topic of research. Fan et al. [36] prepared a Ru-Co-B/γ-Al_2O_3 catalyst, and obtained a cyclohexene yield of 28.8% without any additives in this catalyst. Moreover, the catalyst can be recycled six times without loss in activity and cyclohexene selectivity, indicating the excellent stability of the catalyst. This is shown in Fig. 3.

3.5 Pretreatment

The pretreatment often used is a process where the catalyst is kept for 1 h or more in the presence of $ZnSO_4$ but in the absence of benzene under reaction conditions. The industrial operation requires 22 h [54]. Our group investigated the effects of the pretreatment on the catalytic performance of the Ru-Fe-B/ZrO_2 catalyst and found that the activity decreased and cyclohexene selectivity increased significantly after the pretreatment [50]. $\gamma_{40} > 100$ and $S_{HE}(40) > 80\%$ are required in industrial production in order to reduce the burden of post-treatment, where γ_{40} is the activity index and represents the mass of benzene converted by 1 g of catalyst per hour at the benzene conversion of 40%, and $S_{HE}(40)$ is the cyclohexene selectivity at the benzene conversion of 40% [50]. The values of $\gamma_{40} = 351.6$ and $S_{HE}(40) = 83.33\%$ obtained over the Ru-Fe-B/ZrO_2 catalyst completely satisfied the industrial demand. We proposed the roles of the pretreatment were the following three. (1) After the pretreatment, hydrogen was preferentially adsorbed on the most active sites and benzene can be only adsorbed on the moderately active sites. This benefits the activation of benzene and also the desorption of cyclohexene [50]. (2) The pretreatment resulted in the passivation and structural stability of the catalyst, which prolonged the life of the catalyst [55]. (3) The pretreatment shifted the pore distribution to bigger pores, which promoted the desorption of cyclohexene and improved cyclohexene selectivity [55].

4 Modifiable character

Modifiable character here means the modification of the activity and selectivity by adding an amount of acidic or basic substance in order to compensate for deviations from the normal activity and selectivity caused by factors such as long time run and fluctuation of the reaction conditions to keep the normal operation of the catalyst [30,56]. Our group investigated the effects of the dosage and feeding method of ZnO and H_2SO_4 on the performance of the Ru-Fe-B/ZrO_2 catalyst [35]. The results showed that cyclohexene selectivity increased and activity decreased with increased ZnO dosage. Activity increased and cyclohexene selectivity decreased with increased H_2SO_4 dosage. Different feeding methods of ZnO or H_2SO_4 exerted definite influence on the performance of the catalyst, but the degrees of influence were different. Moreover, the activity and cyclohexene selectivity of the catalyst can be reversibly modified by adding ZnO or H_2SO_4 into the slurry. We speculated that ZnO or H_2SO_4 can reversibly modify the content of Zn chemisorbed on the surface of the catalyst and the distribution, morphology, and electron density of the Ru active sites were changed. The mode of chemisorption was the leading cause fort the difference in the catalytic performances with respect to the two feeding methods of ZnO or H_2SO_4. It is also the main reason why the activity and the selectivity during the modifying test were different from that during the blank test.

5 Pilot test of the catalyst

5.1 Batch pilot test

In 2002, supported by the Innovation Fund for Technology Based Firms and in cooperation with enterprises, our group completed the scaleup of the preparation of the Ru-Fe-B/ZrO_2 catalyst for a pilot test and successfully tested the catalytic technology in a 50 L batch reactor [52]. The results indicated that both the activity and cyclohexene selectivity of the catalyst increased with the increase of Zn^{2+} concentration from 0.5 to 0.6 mol/L. The addition of dispersant ZrO_2 can improve both the activity and cyclohexene selectivity for the concentration of Zn^{2+} below 0.5 mol/L. The optimal dosage of ZrO_2 was $m(\mathrm{Cat})/m(ZrO_2) = 1:2$. A larger dosage led to a slight increase in the activity and a large decrease in the cyclohexene selectivity. A cyclohexene selectivity of 80% at a benzene conversion of 40% was achieved over the catalyst pretreated 12 h under the optimal conditions: reaction temperature of 130–135 ^oC, H_2 pressure of 4.5–5.0 MPa, Zn^{2+} concentration of 0.5 mol/L, $V(H_2O):V(C_6H_6) = 2:1$ and $m(\mathrm{Cat})/m(ZrO_2) = 1/2$, which approached the laboratory level.

5.2 Continuous pilot test

In cooperation with an enterprise, our group investigated the activity and cyclohexene selectivity, modifiable character, regeneration, and lifetime of the Ru-La-B/ZrO_2 catalyst in a 100 L stainless steel autoclave shown in Fig. 4 [37,38,55]. Figure 5 shows the activity and cyclohexene selectivity over the Ru-La-B/ZrO_2 catalyst and Ru-Zn catalyst, respectively, at 170 h. The activity of the Ru-La-B/ZrO_2 catalyst was higher by above 10% before 100 h. In the 100–170 h period, the activities of both were close. The cyclohexene selectivity gradually increased with time and the cyclohexene selectivity of the Ru-La-B/ZrO_2 catalyst was obviously higher than that of the Ru-Zn catalyst after 40 h. It should be noted that the Ru loading of the former was 0.18 kg, which was 40% that of the latter.

In this unit we also carried out the detailed investigation of the regeneration of the Ru-La-B/ZrO_2 catalyst [38,55]. The TEM results indicated that the deactivation of the catalyst was mainly attributable to the agglomeration of the particles and crystallization of the amorphous alloy. Contents of Zn^{2+} and Fe^{2+}, dissolved from the inner wall of the unit, in the reaction slurry and on the surface of the catalyst at different reaction times were detected. The results suggested that the cumulative adsorption of Zn^{2+} and especially Fe^{2+} also led to the deactivation of the catalyst, and thus a washing method was proposed. Table 5 showed the activity and cyclohexene selectivity of the catalyst before and after regeneration with different washing methods. The acid-washing methods can recover the activity and cyclohexene selectivity of the catalyst. Washing with 2.0 mol/L HCl can remove more Fe^{2+} and all Zn^{2+} from the analysis of the contents of Zn^{2+} and Fe^{2+} in the wash water and gave the best catalyst from the regeneration.

Figure 6 shows the activity and cyclohexene selectivity after the addition of the regenerated catalyst (a) and during the 340–360 h period. As can be seen from Fig. 6(a), the activity after the regeneration rose 30.6% and was maintained above 24.0% for 14 h. Cyclohexene selectivity first decreased and increased gradually with reaction time. The activity of the catalyst can be stabilized at above 20% and cyclohexene selectivity maintained above 55% for 466 h by the regeneration and modification as shown in Fig. 6(b). That is, a completely catalytic system using the amorphous alloy catalyst for benzene selective hydrogenation to cyclohexene has been established by the pilot test.

6 Conclusions and prospects

A Ru-M-B/ZrO_2 catalyst is better than the present industrial Ru-Zn catalyst because of its higher activity and excellent cyclohexene selectivity, higher utilization of Ru and simpler preparation processes. This Ru-Fe-B/ZrO_2 catalyst is the most attractive of the catalysts for the selective hydrogenation of benzene to cyclohexene. However, results from a continuous pilot plant are less than satisfactory and showed some differences with those from a batch pilot plant. The investigation of the differences between the continuous technology and batch technology and the improvement of the catalyst and technology conditions to give better performance and the industrial application of the amorphous alloy catalyst are the main present tasks. The use of the amorphous alloy catalyst without any additive only gave a low cyclohexene yield of 28.8% and low cyclohexene selectivity, so this technology is another important research project to develop a high stability of the catalyst to go with the low demand on the reactor and its simple operation.

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