

单层分散型 Ru-Zn 催化剂及其催化苯选择加氢制环己烯的性能

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摘要: 采用共沉淀法制备了一系列不同 Zn 负载量的 Ru-Zn 催化剂. XRD 和 XPS 结果表明, 催化剂中的 Zn 大部分以 ZnO 形式存在, 在加氢过程中催化剂表面的 ZnO 可以与浆液中的 Zn^{2+} 形成碱式硫酸锌盐. 随催化剂中 Zn 负载量的增加, 碱式硫酸锌盐的量也增加, 这导致催化剂活性降低和环己烯选择性升高. 当 Zn 负载量为 8.6% 时, 加氢后碱式硫酸锌盐在 Ru-Zn 催化剂表面上接近单层分散态. 单层分散型 Ru-Zn 催化剂催化性能最佳, 该催化剂在 140 °C, 5 MPa H_2 下和 0.6 mol/L 硫酸锌溶液中预处理 22 h 后, 反应 20 min, 苯转化率 84.4% 时, 环己烯选择性为 69.8%.

关键词: 单层分散型; 钌; 锌; 苯; 选择加氢; 环己烯

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Monolayer Dispersed Ru-Zn Catalyst and Its Performance in the Selective Hydrogenation of Benzene to Cyclohexene

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Abstract: A series of Ru-Zn catalysts with different Zn loadings were prepared by co-precipitation. X-ray diffraction and X-ray photoelectron spectroscopy results showed that a large part of the Zn in the Ru-Zn catalysts were present in the form of ZnO and the ZnO on the catalyst surface could react with $ZnSO_4$ in the slurry to form a basic zinc sulfate salt during hydrogenation. The content of the basic salt increased with an increase in the Zn loading of the catalysts. This resulted in a decrease in catalyst activity and an increase in selectivity for cyclohexene. When the Zn loading was 8.6%, the basic salt dispersion was close to monolayer dispersion on the catalyst surface. When the catalysts were pretreated in the presence of 0.6 mol/L $ZnSO_4$ solution at 140 °C and at 5 MPa H_2 , a cyclohexene selectivity of 69.8% and a benzene conversion of 84.4% was achieved after 20 min.

Key words: monolayer dispersion; ruthenium; zinc; benzene; selective hydrogenation; cyclohexene

由苯出发经环己烯制备尼龙-6 和尼龙-66 具有安全、节能和环境友好等特点, 一直为人们所关注^[1]. 1989 年, 日本旭化成公司利用无负载 Ru-Zn 催化剂和纳米 ZrO_2 分散剂率先实现了苯选择加氢的工业化, 当苯转化率为 40% 时, 环己烯选择性为 80%^[2,3]. 该公司曾将该技术转让我国, 然而相关催化技术却鲜有报道. 因此, 开展该过程的催化剂研制和反应体系研究具有重要意义.

助剂对催化剂的性能有重要影响. 文献[2,4~11]

报道, K, Fe, Co, Ce, Ba, La 和 Zn 等助剂可显著提高环己烯选择性. 其中 Zn 被认为是最好的助剂. 文献[10,11]认为催化剂前体中的 ZnO 或还原浆液中的 Zn^{2+} 可以被从 Ru 上溢流的 H 还原为金属 Zn, 金属 Zn 原子与 Ru 的相互作用导致催化剂活性降低和环己烯选择性升高. 文献[11]还证实金属 Zn 原子在 Ru 基催化剂中存在最优负载量, 并且该值与加氢反应时水相中的 Zn^{2+} 浓度密切相关. 然而文献并未指出确定 Zn 最优负载量的方法及催化剂中 Zn 与浆液中

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Zn²⁺之间究竟存在何种联系.

单层分散型催化剂具有优越的催化性能^[12]. 本文制备了一系列不同 Zn 负载量的 Ru 基催化剂, 明确了单层分散型 Ru-Zn 催化剂的特征, 考察了其催化性能, 并探讨了催化剂中 Zn 与浆液中 Zn²⁺之间的关系.

催化剂参照文献[13]方法制备. 将一定量 RuCl₃·3H₂O 和 ZnSO₄·7H₂O 溶于 200 ml 蒸馏水中, 搅拌下快速加入 200 ml 30% NaOH 溶液, 于 80 °C 下搅拌 4 h. 静置后弃去上层清液, 得到的黑色固体用 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 5.0 MPa H₂ 压和 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 负载量的催化剂分别记作 Ru-Zn(x), x 为原子吸收光谱测得的催化剂中 Zn 含量.

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 和 280 ml H₂O. 在 H₂ 压力为 5.0 MPa 和搅拌速率为 800 r/min 的条件下预处理 22 h. 然后, 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. 催化剂直接加氢省去 22 h 的预处

理, 其它条件同上.

样品物相分析在 PAN Nalytical 公司的 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 5°~90°, 扫描步长 0.03°. 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. 催化剂表面 Zn 的价态用 PHI Quantera SXM 型 X 射线光电子能谱 (XPS) 仪测定, Al K_α (E_b = 1486.6 eV) 为辐射源, 分析室真空度 6.7 × 10⁻⁸ Pa. 以石墨 C 1s (E_b = 284.8 eV) 为标准进行校正.

图 1 为不同 Zn 负载量的 Ru-Zn 催化剂加氢前后的 XRD 谱. 从图 1(a) 可以看出, 所有催化剂在 2θ = 38.4°, 44.0°, 58.3°, 69.4°, 78.4° 和 84.7° 等处出现了衍射峰, 归属为 Ru (JCPDS No.010-070-0274) 特征峰. 利用最强衍射峰 2θ = 44.0° 的半峰宽及 Scherrer 公式计算出催化剂中 Ru 微晶尺寸分别为 4.1, 4.3, 3.8, 3.7, 3.9, 4.3, 4.0, 3.8 和 3.8 nm. 除此之外, Ru-Zn(29.1%) 样品还在 2θ = 31.8°, 34.4°, 36.3°, 47.5°, 56.6°, 62.9° 和 68.0° 处出现新的衍射峰, 归属于 ZnO (JCPDS No.010-070-2551) 特征峰. 这说明催化剂表面部分 Zn 以 ZnO 的形态存在. 由图 1(b) 可见, 与 ZrO₂ 对比, 除 2θ = 8.09°, 16.2° 和 44.0° 等处衍射峰外, 其它样品的衍射峰均为 ZrO₂ 的特征峰. 44.0° 处极微弱且弥散的衍射峰归属于 Ru (JCPDS No.010-070-0274) 特征峰, 这说明 Ru 微晶尺寸很小. 2θ = 8.09° 和 16.2° 处的

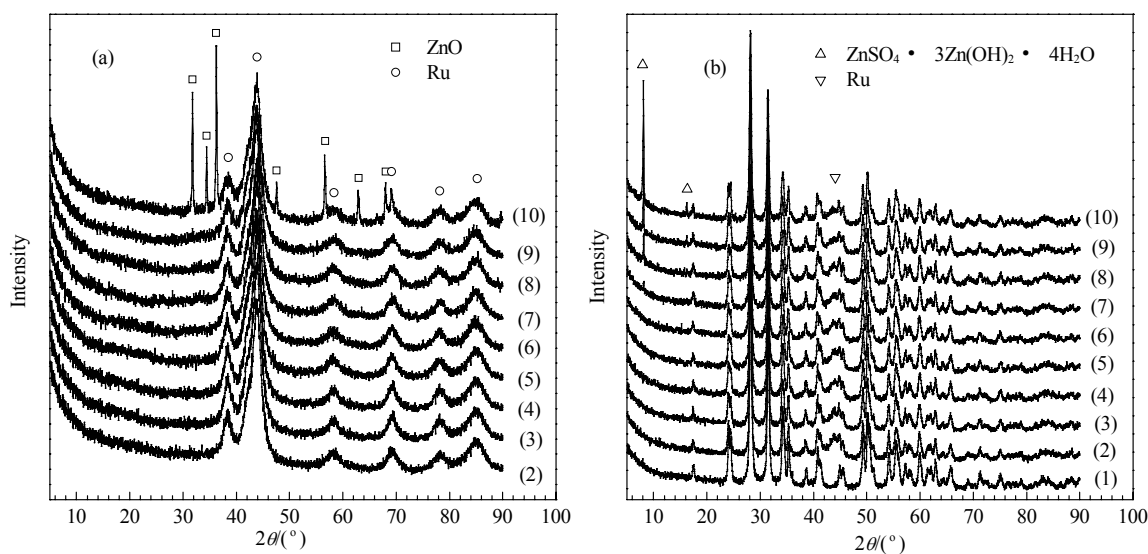


图 1 不同 Zn 负载量的 Ru-Zn 催化剂加氢前后的 XRD 谱

Fig. 1. XRD patterns of the Ru-Zn catalysts with different Zn loadings before (a) and after hydrogenation (b). (1) ZrO₂; (2) Ru-Zn(0); (3) Ru-Zn(2.6%); (4) Ru-Zn(5.2%); (5) Ru-Zn(7.7%); (6) Ru-Zn(8.6%); (7) Ru-Zn(9.6%); (8) Ru-Zn(12.4%); (9) Ru-Zn(14.9%); (10) Ru-Zn(29.1%).

衍射峰归属于 $\text{ZnSO}_4 \cdot 3\text{Zn}(\text{OH})_2 \cdot 7\text{H}_2\text{O}$ (JCPDS No. 00-009-0204) 特征峰, 这说明催化剂表面的 ZnO 与浆液中的 $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 生成了碱式硫酸盐. 从图 1(b) 还可以看出, 随着样品中 Zn 负载量的增加, $2\theta \approx 8.1^\circ$ 处衍射峰从无到有并逐渐增强, 与 Zn 负载量逐渐一致. 图 2 为 $\text{Ru-Zn}(8.6\%)$ 样品加氢前后的 XPS 谱. 由图可见, 反应前 $\text{Ru-Zn}(8.6\%)$ 催化剂中 $\text{Zn } 2p_{3/2}$ 和 $\text{Zn } 2p_{1/2}$ 的电子结合能分别为 1021.8 和 1044.9 eV, 与文献[14]报道的 ZnO 和 Ag/ZnO 催化剂中 $\text{Zn } 2p_{3/2}$ 的电子结合能 1021.9 和 1021.8 eV 完全一致, 这说明 $\text{Ru-Zn}(8.6\%)$ 样品中有部分 Zn 以 ZnO 形式存在. 然而除 $\text{Ru-Zn}(29.1\%)$ 样品外其它样品上并未发现 ZnO 特征峰, 其原因可能是 ZnO 量少、高度分散或微晶尺寸小于检出限.

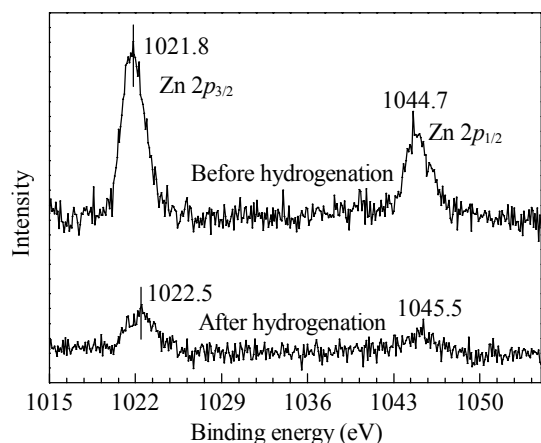


图 2 $\text{Ru-Zn}(8.6\%)$ 催化剂样品加氢反应前后的 XPS 谱

Fig. 2. XPS spectra of the $\text{Ru-Zn}(8.6\%)$ sample before and after hydrogenation.

当 Zn 负载量为 8.6% 时, $\text{ZnSO}_4 \cdot 3\text{Zn}(\text{OH})_2 \cdot 7\text{H}_2\text{O}$ 在活性组分 Ru 和分散剂 ZrO_2 上接近单层分散态. 这是单层分散型 Ru-Zn 催化剂的重要特征. 很明显, $\text{ZnSO}_4 \cdot 3\text{Zn}(\text{OH})_2 \cdot 7\text{H}_2\text{O}$ 为催化剂与浆液中 Zn^{2+} 相互作用的纽带. 我们推测催化剂中 Zn 负载量和浆液中 Zn^{2+} 浓度都影响碱式硫酸盐的生成和组成, 进而影响催化剂的性能. 这与文献[11]报道的最优 Zn 负载量与浆液中 Zn^{2+} 密切相关的结论相符. 由图 2 可知, $\text{Ru-Zn}(8.6\%)$ 催化剂加氢后 $\text{Zn } 2p_{3/2}$ 和 $\text{Zn } 2p_{1/2}$ 的电子结合能分别 1022.5 和 1045.5 eV, 比加氢前催化剂相应结合能分别高 0.7 和 0.6 eV. 这进一步证实了加氢过程中催化剂表面的 Zn 大部分仍以 Zn^{2+} 存在并未被还原. 同时说明催化剂表面的 ZnO 和浆液中

Zn^{2+} 及分散剂 ZrO_2 之间存在较强的相互作用, 改变了催化剂表面 Zn 的电子状态.

图 3 给出了不同 Zn 负载量的 Ru-Zn 催化剂的催化性能. 可以看出, 随着 Zn 负载量的增加, 催化剂活性逐渐降低, 环己烯选择性逐渐升高, 与 Hu 等^[10] 报道的结论一致. 不加 $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 的实验同样被考察, 结果表明, 反应 10 min 时 $\text{Ru-Zn}(9.6\%)$ 催化剂上苯转化率为 98.2% 的情况下, 环己烯选择性仅为 1.4%, 比纯 Ru 催化剂苯转化 99.2% 时环己烯选择性 (0.3%) 仅略有提高. 而在 $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 存在下, 前者在苯转化 45.1% 时环己烯选择性达 80.9%. 这表明只有在催化剂中的 Zn 和浆液中的 $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 的协同作用下 Ru-Zn 催化剂才能表现出优越的环己烯选择性. $\text{ZnSO}_4 \cdot 3\text{Zn}(\text{OH})_2 \cdot 7\text{H}_2\text{O}$ 在苯选择加氢反应中起着至关重要的作用: (1) $\text{ZnSO}_4 \cdot 3\text{Zn}(\text{OH})_2 \cdot 7\text{H}_2\text{O}$ 为难溶性盐, 比 ZnSO_4 更易化学吸附在催化剂和分散剂 ZrO_2 的表面上. 其含有的大量 Zn^{2+} 和结晶水, 可以极大地增加了 Ru 的亲水性, 使环己烯选择性升高^[15]; (2) 化学吸附在 Ru 上的 $\text{ZnSO}_4 \cdot 3\text{Zn}(\text{OH})_2 \cdot 7\text{H}_2\text{O}$ 可以占

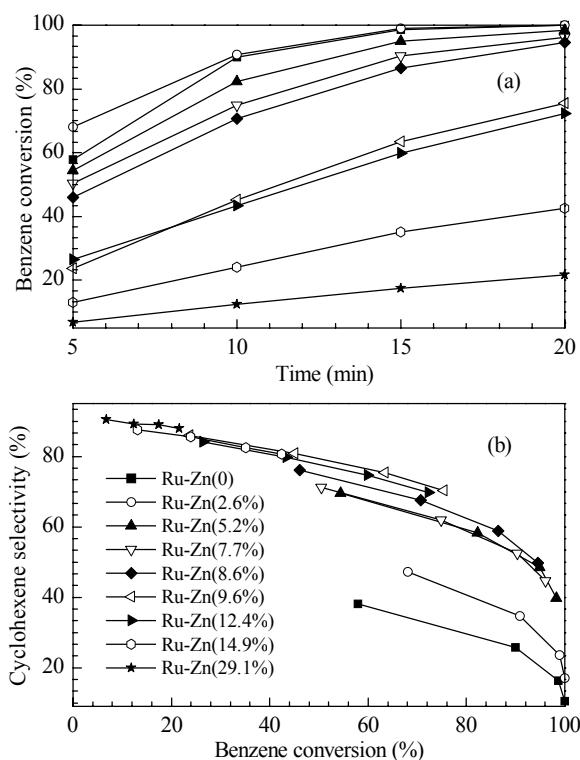


图 3 不同 Zn 负载量 Ru-Zn 催化剂上的苯转化率和环己烯选择性

Fig. 3. Benzene conversion (a) and cyclohexene selectivity (b) on the Ru-Zn catalysts with different Zn loadings.

据不适宜生成环己烯的活性位; (3) $\text{ZnSO}_4 \cdot 3\text{Zn}(\text{OH})_2 \cdot 7\text{H}_2\text{O}$ 中 Zn^{2+} 与活性组分 Ru 之间的电子相互作用可以改变 Ru 的电子结构. 此外, 有部分 ZnO 被 Ru 上溢流的 H 还原为 Zn, Zn 原子修饰的 Ru 基催化剂适宜于苯选择加氢制环己烯^[10,11]. 但由于 Zn 的微晶尺寸很小, 且易与 Ru 形成固溶体^[13], 因此在 XRD 谱上未检测到 Zn 的特征峰. 这些是导致随 Zn 负载量增加催化剂活性降低和环己烯选择性增加重要原因. 值得一提的是, 当 Zn 负载量从 8.6% 增加到 9.6% 时催化剂活性急剧降低, 而环己烯选择性仅略有升高. 这与 Zn 负载量为 8.6% 时 $\text{ZnSO}_4 \cdot 3\text{Zn}(\text{OH})_2 \cdot 7\text{H}_2\text{O}$ 的单层分散有关.

为进一步考察单层分散型 Ru-Zn 催化剂的性能, 本文对 Zn 负载量为 7.7%, 8.6% 和 9.6% 的催化剂进行了预处理, 结果见图 4. 可以看出, 预处理后, Ru-Zn(8.6%) 催化剂活性适中, 环己烯选择性最高, 且随苯转化率的升高环己烯选择性缓慢降低. 在该催化剂上, 苯转化率为 84.4% 时, 环己烯选择性为 69.8%. Ru-Zn(7.7%) 催化剂活性虽然比 Ru-Zn(8.6%)

的较高, 但环己烯选择性却比后者的低得多. 而 Ru-Zn(9.6%) 催化剂虽然初始选择性比 Ru-Zn(8.6%) 的高, 但活性较后者低, 且随苯转化率的增加环己烯选择性降低的程度明显比后者快. 单层分散型 Ru-Zn 催化剂性能最佳, 这与文献[12]报道是一致的. 说明预处理的作用有: (1) 预处理后, H 和苯分别优先吸附在强和中等活性中心上, 此时苯既易被活化, 中间产物又易脱附, 这导致催化剂活性下降和选择性升高^[16]; (2) 使催化剂钝化和结构稳定化, 延长催化剂的使用寿命^[17]; (3) 使催化剂孔径向大孔方向移动, 有利于环己烯的溢出, 环己烯选择性提高^[17]. 此外, 在 ZnSO_4 中预处理还可能使生成的碱式硫酸锌盐稳定化, 更牢固的吸附在催化剂的表面.

总之, 碱式硫酸锌在 Ru-Zn 催化剂表面上单层分散时, Ru-Zn 催化剂催化苯选择加氢制环己烯反应性能最佳. 这为高活性和高选择性苯选择加氢催化剂和其它选择加氢(如炔烃加氢生成烯炔等)催化剂的研发提供了一条新的思路.

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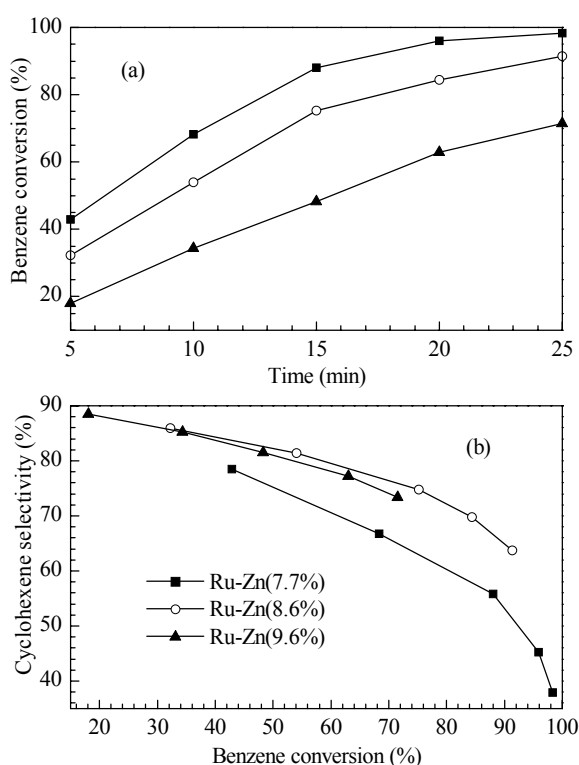


图 4 不同 Zn 负载量的 Ru-Zn 催化剂预处理后苯转化率和环己烯选择性

Fig. 4. Benzene conversion (a) and cyclohexene selectivity (b) on the catalysts pretreated with different Zn loadings.

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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 it is an environmentally benign process with a good atom economy [1]. In 1989, the Asahi Chemical Industry Co. industrialized the process for producing cyclohexene from the selective hydrogenation of benzene based on unsupported Ru-Zn catalysts and nanosized ZrO₂ as a dispersant, and a cyclohexene selectivity of 80% as well as a benzene conversion of 40% were obtained [2,3]. The technology has been sold in China by Asahi Chemical Industry Co. but the details of this process have never been released. Therefore, scientific studies on catalyst preparation and modification are needed.

Promoters greatly impact the performance of catalysts. It has been reported that promoters such as K, Fe, Co, Ce, Ba, La, and Zn can remarkably enhance the selectivity for cyclohexene [2,4–11] and Zn has been regarded as the best promoter. It has been proposed that the ZnO in the precursor of the catalyst or the Zn²⁺ chemisorbed on metallic Ru can be reduced to their elemental state by hydrogen atoms, which spill over from metallic Ru. The interaction between metallic zinc and metallic Ru can lead to a decrease in the activity of the catalyst and an increase in cyclohexene production. It has also been suggested that an optimal Zn loading exists for the Ru-based catalyst and it is closely related to the concentration of Zn²⁺ in the slurry [11]. However, methods to determine the optimal Zn loading as well as the relationship between the Zn in the catalysts and Zn²⁺ in the slurry have not been reported.

Monolayer dispersed catalysts have excellent catalytic performance [12]. We prepared a series of Ru-based catalysts with different Zn loadings. The features of the monolayer dispersed Ru-Zn catalysts were determined, their catalytic performance was investigated and the link between the Zn in the catalysts and Zn²⁺ in the slurry were clarified.

The Ru-Zn catalysts were prepared according to a literature procedure [13]. A desired amount of RuCl₃·H₂O and ZnSO₄·7H₂O were dissolved in 200 ml H₂O with agitation. To the stirred solution, 200 ml 20% NaOH solution was

added instantly and the resulting mixture was agitated for an additional 4 h at 80 °C. The mixture was left to stand and the obtained black precipitate 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 5% NaOH solution and charged into a 1 L Teflon-lined autoclave. Hydrogen was introduced into the autoclave to raise the total internal pressure to 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 obtained black powder was washed three times with 5% NaOH and then with water until neutral to give the desired Ru-Zn catalysts. The amount of ZnSO₄·7H₂O was adjusted to give the desired Zn loading. The catalysts with different Zn loadings were denoted as Ru-Zn(*x*) where *x* indicates the Zn loading, as determined by atomic absorption spectrometry (AAS).

The selective hydrogenation of benzene was performed in a 1 L hastelloy-lined autoclave. The catalyst (1.96 g) was pretreated for 22 h in the presence of 280 ml H₂O containing 49.2 g ZnSO₄·7H₂O and 9.8 g ZrO₂ at 150 °C, and with a H₂ pressure of 5 MPa as well as a stirring rate of 800 r/min. 140 ml of benzene was then added to the reactor at 150 °C and the stirring rate was increased to 1400 r/min to exclude any external diffusion effect and the reaction time began. A small amount of reaction mixture was sampled every 5 min and sent for gas chromatographic analysis (FID detector), and the benzene conversion and cyclohexene selectivity were calculated. The direct hydrogenation followed the above operation except for a 22 h pretreatment.

Powder X-ray diffraction (XRD) patterns were acquired on a PANalytical X'Pert PRO instrument. The X-ray tube was operated at 40 kV and 40 mA. The spectra were collected in the 2θ range from 20°–80° with a step of 0.03°. AAS was performed on a Perkin Elmer Analyst 300 instrument operating at λ = 213.9 nm and with a slit width of 0.20 nm to determine the Zn loading. X-ray photoelectron spectroscopy (XPS) was used to determine the chemical state of the surface Zn on a PHI Quantera SXM instrument with a base pressure of 6.7 × 10⁻⁸ Pa. Al K_α (E_b = 1 486.6 eV) was used as the excitation radiation. Calibration of the spectra was done on a spurious C 1s peak and it was fixed at 284.5 eV.

Figure 1 shows the XRD patterns of the Ru-Zn catalysts before and after hydrogenation. Figure 1 shows that the patterns of all samples contain six characteristic peaks of metallic Ru at 2θ values of 38.4°, 44.0°, 58.3°, 69.4°, 78.4°, and 84.7° (JCPDS 010-070-0274). The crystallite sizes of the Ru in the catalysts estimated from the strongest peak broadening at 44.0° using the Scherrer equation are 4.1, 4.3, 3.8, 3.7, 3.9, 4.3, 4.0, 3.8, and 3.8 nm, respectively. Apart from the above-mentioned peaks the Ru-Zn(29.1%) catalyst has seven new peaks at 2θ values of 31.8°, 34.4°, 36.3°, 47.5°, 48.5°, 50.5°, and 52.5°.

56.6°, 62.9°, and 68.0° that correspond to the ZnO phase (JCPDS 010-070-2551). This indicates that a part of the Zn in the catalysts exist in the form of ZnO. By comparison with ZrO_2 all the peaks are assigned to the main phase except for the peaks at 2θ values of 8.09°, 16.2°, and 44.0°, as shown in Fig. 1. The wide and weak peak at the 2θ value of 44.0° corresponds to the metallic Ru phase (JCPDS 010-070-0274) indicating a small crystallite size for Ru. The peaks at 2θ values of 8.09° and 16.2° are attributed to the $\text{ZnSO}_4 \cdot 3\text{Zn}(\text{OH})_2 \cdot 7\text{H}_2\text{O}$ phase (JCPDS 00-009-0204). This suggests that the ZnO in the catalyst reacted with ZnSO_4 in the slurry to form a basic zinc sulfate salt. Peaks of the basic zinc sulfate salt appear and gradually increase in intensity indicating that the amount of this basic salt increases with the Zn loading. Figure 2 shows XPS spectra of the Ru-Zn(8.6%) sample before and after hydrogenation. The binding energies of Zn $2p_{3/2}$ and Zn $2p_{1/2}$ in the Ru-Zn(8.6%) sample before hydrogenation was 1021.9 and 1044.9 eV, respectively, which is consistent with the binding energies of Zn $2p_{3/2}$ in the ZnO and Ag/ZnO catalysts at 1021.9 and 1021.8 eV, respectively, as reported in the literature [14]. This indicates that a part of the Zn in the Ru-Zn(8.6%) sample exists as ZnO. However, ZnO was not detected by XRD in the other samples except for the Ru-Zn(29.1%) sample because of its low quantities and high dispersion while the smaller crystallite sizes were under the detectable limit of the instrument.

At a Zn loading of 8.6% the basic salt dispersion is close to a monolayer dispersion. This is one of the important features of the monolayer dispersed Ru-Zn catalyst. Obviously, the basic salt is composed of a bond between the ZnO in the catalysts and the ZnSO_4 in the slurry. The Zn loading and the concentration of Zn^{2+} in the slurry can affect the formation and the composition of the basic salt and subsequently the performance of the catalysts is influenced. This is in good agreement with the conclusions reported in the literature about the optimal Zn loading being closely related to the concentration of Zn^{2+} in the slurry. The binding energy of Zn $2p_{3/2}$ and Zn $2p_{1/2}$ in the Ru-Zn(8.6%) sample after hydrogenation was found to be 1022.5 and 1045.5, respectively, which is 0.7 and 0.6 eV higher than that before hydrogenation, as shown in Fig. 2. We further confirm that a large part of the Zn is still present in the form of Zn^{2+} and cannot be reduced further. This indicates that there is a strong interaction between ZnO on the catalyst surface and Zn^{2+} in the slurry as well as the dispersant ZrO_2 , which results in a change in the Zn electronic state.

The catalytic performance of the Ru-Zn catalysts with different Zn loadings for the selective hydrogenation of benzene to cyclohexene is shown in Fig. 3. As can be seen, the activity of the catalysts decreases and the cyclohexene selectivity increases with an increase in Zn loading, which is consistent with the results reported by Hu et al. [13]. A test

without the addition of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ was also carried out. The results showed that on the Ru-Zn(9.6%) catalyst the cyclohexene selectivity is only 1.4% and the benzene conversion is 98.2% after 10 min and this was slightly higher than the cyclohexene selectivity (1.4%) and the benzene conversion (99.2%) over the Ru-Zn(0) catalyst. However, over the former catalyst the cyclohexene selectivity reached 80.9% at a benzene conversion of 45.1% in the presence of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$. This indicates that the Ru-Zn catalyst gives excellent cyclohexene selectivity with the synergic action of Zn on the catalyst surface and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ in the slurry. Therefore, $\text{ZnSO}_4 \cdot 3\text{Zn}(\text{OH})_2 \cdot 7\text{H}_2\text{O}$ plays a key role in the selective hydrogenation of benzene to cyclohexene: (1) $\text{ZnSO}_4 \cdot 3\text{Zn}(\text{OH})_2 \cdot 7\text{H}_2\text{O}$ is an insoluble salt and is more easily chemisorbed on the catalyst surface than ZnSO_4 . The large amount of Zn^{2+} and rich crystal water can especially enhance the hydrophilicity of the catalyst and this leads to an increase in cyclohexene selectivity [15]; (2) $\text{ZnSO}_4 \cdot 3\text{Zn}(\text{OH})_2 \cdot 7\text{H}_2\text{O}$ can block the active sites that are not suitable for the formation of cyclohexene; (3) The interaction between Zn^{2+} in $\text{ZnSO}_4 \cdot 3\text{Zn}(\text{OH})_2 \cdot 7\text{H}_2\text{O}$ and the active Ru component can modify the electronic structure of Ru. The ZnO or Zn^{2+} that are chemisorbed on the Ru active centers can be reduced to their elemental state by hydrogen atoms, which spilled over from metallic Ru. Ru-based catalysts modified by metallic Zn are suitable for the selective hydrogenation of benzene to cyclohexene [10,11]. However, no Zn peaks were detected because of the small crystallite sizes and the formation of a Ru-Zn solid solution [18]. All of these are important reasons that lead to a decrease in the activity of the catalysts and an increase in cyclohexene selectivity with an increase in the Zn loading. When the Zn loadings increase from 8.6% to 9.6%, the activity of the catalysts decrease drastically, however, the selectivity for cyclohexene increases slightly. This contributes to the monolayer dispersion of the basic salts on the catalyst with a Zn loading of 8.6%.

To further verify the catalytic performance because of the monolayer dispersion of the Ru-Zn catalyst, catalysts with the Zn loading of 7.7%, 8.6%, and 9.6% were pretreated and the results are shown in Fig. 4. After the pretreatment, the catalysts with a Zn loading of 8.6% exhibited moderate activity and the best cyclohexene selectivity. Moreover, cyclohexene selectivity decreased slowly with an increase in benzene conversion. A cyclohexene selectivity of 69.8% and a benzene conversion of 84.4% were obtained for this catalyst. The activity of the catalyst with a Zn loading of 7.7% was higher than that of the catalyst with a Zn loading of 8.6% while the cyclohexene selectivity of the latter was much higher than that of the former. Although the initial selectivity of the catalyst with a Zn loading of 9.6% was higher than that of the catalyst with a Zn loading of 8.6%, the latter had a higher activity than the former. Moreover, the cyclohexene

selectivity of the latter decreased more slowly than that of the former with an increase in benzene conversion. This indicates that the monolayer dispersion catalyst had the best catalytic performance, which is in agreement with reference [12]. This also indicates that the role of the pretreatment is as follows: (1) After the pretreatment, hydrogen was preferentially adsorbed on the most active sites and benzene was only adsorbed on the moderately active sites. This benefited the activation of benzene and also the desorption of cyclohexene [16]; (2) The pretreatment resulted in the passivation and structural stability of the catalyst, which prolonged the life of the catalyst [17]; (3) The pretreatment shifted the pore distribution to larger pores, which promoted the desorption of cyclohexene and improved cyclohexene selectivity [17]. The

pretreatment with ZnSO_4 enhanced the stability of the basic sulfate salt and caused the basic sulfate salt to adsorb more strongly onto the catalyst surface.

Above all, the catalyst gave the best performance for the selective hydrogenation of benzene to cyclohexene when the basic sulfate salt was dispersed over the Ru-Zn catalyst surface as a monolayer. This provides a clear path for the development of novel catalysts with good activity and excellent selectivity for the selective hydrogenation of benzene to cyclohexene and for other selective hydrogenations (such as the selective hydrogenation of alkynes to alkenes).

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