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博　士　学　位　论　文

Ru-TM/TMO/C 催化剂纳米结构的设计，制备及其催化芳烃加氢性能的研究

(TM = Ni、Co；TMO = NiO、Co_3O_4)

Design and Synthesis of Nanostructure of the Ru-TM/TMO/C Catalysts and Investigation of Their Catalytic Performance in Aromatic Hydrogenation

(TM = Ni、Co；TMO = NiO、Co_3O_4)

朱丽华

指导教师姓名：陈秉辉 教授
专　业　名　称：工　业　催　化
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评　　阅　　人：＿＿＿＿＿

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摘　要

为了提高多相催化反应中催化剂的活性、选择性与稳定性，合理设计催化剂对实现反应物高效且有选择的吸附与活化十分关键。由于大多数反应都涉及到两种或多种反应物，最理想的催化剂应可对应不同反应物，具有不同的活性位将其吸附与活化。芳烃是一种重要的化工原料和平台化合物，其重要的产品延伸是芳环加氢产物。以苯催化加氢制环己烷为例，环己烷不仅是生产环己酮、环己醇、己内酯、己内酰胺、尼龙-6 与尼龙-66 等的重要原料，还是一种优良的有机溶剂。因此，合理设计与开发高效且低成本芳烃加氢催化剂显得极其重要，同时对该加氢反应催化剂的研究，可获得一些加氢催化剂研究的共性问题，颇具学术研究和工业应用价值。

本研究第一部分内容是：以炭黑为催化剂载体，制备小岛状贵金属 Ru 负载于 Ni/NiO 纳米颗粒负载型催化剂（Ru-Ni/NiO/C），该催化剂具有协同的多活性位 Ru、Ni 与 NiO，可高效催化芳烃加氢反应。以此为基础，将 Ni 用过渡金属 Co 替代，成功研制出具有更高催化加氢活性的 Ru-Co/Co_3O_4/C 催化剂。两种金属的协同作用，给双金属纳米材料带来了一些新的物理化学性质，使得人们对其可控制备与应用产生了极大的兴趣，且双金属在多相催化中有着重要的应用。而影响双金属纳米催化剂活性、选择性与稳定性的主要因素有双金属纳米结构、尺寸与组成。因此，本研究第二部分内容是：以苯加氢制环己烷为模型反应，RuNi/C 为双金属催化剂，研究 RuNi 双金属纳米结构及尺寸与其催化苯加氢制环己烷性能的内在关系。

本文主要获得以下研究结果：

1. 提出了一种设计与制备贵金属与过渡金属氧化物复合的多活性位催化剂的方法。以 Ru-Ni/NiO/C 催化剂的设计为例及苯加氢制环己烷为模型反应，研究发现 Ru-Ni/NiO/C 的催化性能为 Ru-Ni 纳米合金或 Ru/Ni 相分离负载于炭黑（Ru-Ni/C）的 55 倍左右，为传统 Ru/C 的 10~11 倍。通过热重（TG）、X 射线衍射（XRD）、X 射线光电子能谱（XPS）、透射电子显微镜（TEM）、高分辨透射电子显微镜（HRTEM）、球差高角度环形暗场扫描透射像（Cs-HAADF-STEM）、

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X 射线能谱元素面扫（EDS-mapping）与线扫分析（line-scan）、高灵敏度低能离子散射谱（HS-LEIS）及 X 射线吸收近边结构（XANES）和扩展 X 射线吸收精细结构能谱（EXAFS）表征，分析了 Ru-Ni/NiO/C 与 Ru-Ni/C 在纳米结构与原子水平上的异同，证实了 Ru-Ni/NiO/C 催化剂高活性与稳定性主要归因于协同的多活性位（Ru、Ni 与 NiO）。其中，Ru 活性位吸附与活化 H_2、NiO 活性位吸附与活化苯、Ni 活性位起着氢溢流作用“桥梁”将活化了的 H^* 物种转移至活化的苯上。

2. 为了进一步验证上述多活性位分工协同的催化剂设计理念，采用水合肼室温还原法制备了 $Co/Co(OH)_2/C$，化学置换法合成了 $Ru\text{-}Co/Co(OH)_2/C$，$Ru\text{-}Co/Co(OH)_2/C$ 经在 N_2 或 N_2+H_2 中 280 ℃ 焙烧 3 h 分别得 $Ru\text{-}Co/Co_3O_4/C$ 与 Ru-Co/C 催化剂。各种表征证实 $Ru\text{-}Co/Co_3O_4/C$ 催化剂中 Ru 主要以小岛状形式负载于 Co/Co_3O_4 纳米颗粒，而 Ru-Co/C 催化剂主要以 Ru-Co 纳米合金形式存在。苯加氢制环己烷实验结果表明 $Ru\text{-}Co/Co_3O_4/C$ 催化剂催化性能最好，且远远高于 Ru-Co/C 与 Ru/C 催化剂。另外，$Ru\text{-}Co/Co_3O_4/C$ 催化剂的活性是 Ru-Ni/NiO/C 的 5 倍。$Ru\text{-}Co/Co_3O_4/C$ 催化剂高效催化苯加氢制环己烷的根本原因可归结为多活性位的分工协同作用：Ru（活化 H_2）、Co_3O_4（活化苯）及 Co（以氢溢流方式“桥梁”传递已活化的 H^* 物种）。此外，改变 Ru-Co 双金属纳米催化剂的热处理条件成功调控其纳米结构。因此，该研究成果为设计与制备低成本且高活性的芳烃加氢催化剂提供了理论基础。

3. 建立了 RuNi/C 双金属纳米催化剂在 N_2 中热处理条件与其催化苯加氢制环己烷性能之间的内在关系。首先，以炭黑为载体，采用水合肼室温还原与化学置换法制备了 $Ru\text{-}Ni/Ni(OH)_2/C$ 催化剂；其次，改变在 N_2 气氛中的热处理温度（未焙烧、160 ℃、230 ℃、280 ℃、380 ℃、480 ℃、580 ℃ 或 680 ℃），成功调控 RuNi 纳米结构、Ru 与 Ni 的化学态。各表征结果表明：当 $Ru\text{-}Ni/Ni(OH)_2/C$ 在 380 ℃ 以下焙烧时，Ru 主要以还原态（Ru(0)）而 Ni 主要以氧化态形式存在，纳米结构为小岛状 Ru 负载于 Ni/NiO（或 $Ni/Ni(OH)_2$）纳米颗粒；480 ℃-Ru 与 Ni 主要以氧化态（RuO_2 与 NiO）形式存在，纳米结构为 RuO_2 负载于 NiO 纳米颗粒；580 ℃ 以上-Ru 与 Ni 主要以还原态（Ru(0)与 Ni(0)）形式存在，纳米结构为 Ru@thin Ni 核壳结构。最后，建立催化剂催化苯加氢制环己烷活性与其热处

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理条件的关系：Ru-Ni/NiO/C-380 ℃活性为 Ru@thin Ni/C-580 ℃或 680 ℃的 3~4 倍，而 RuO_2/NiO/C-480 ℃对反应几乎没有活性。

4. 为了提高双金属催化剂的催化性能，合理设计与控制其纳米结构是非常有必要的。采用与“2”、“3”中相同的制备方法合成了 $Ru_{0.04}Ni_{0.96}$/C~uncalcined 催化剂（Ru/Ni 原子比 = 0.04/0.96）。改变其在 N_2+H_2 气氛中的焙烧温度成功调变 $Ru_{0.04}Ni_{0.96}$ 纳米结构：Ru-Ni 纳米合金（Ru-Ni nanoalloy）-230 ℃或 280 ℃、Ru@thick Ni 核壳结构（Ru@thick Ni）-480 ℃、小岛状 Ru 负载于 Ni 纳米颗粒（Ru islands-on-Ni particles）-680 ℃，且各种表征均证实了以上不同的纳米结构。各催化剂性能采用苯加氢制环己烷评价，最终建立了 $Ru_{0.04}Ni_{0.96}$/C 双金属催化剂催化苯加氢反应的“构效关系”，Ru-Ni nanoalloy/C 与 Ru islands-on-Ni particles/C 催化性能要远高于 Ru@thick Ni/C。该研究结果为双金属纳米颗粒的结构设计与调变提供了一种简单方法。

5. 采用水热合成与化学置换法，改变水热合成温度获得不同平均粒径的 Ru-Ni/NiO 纳米颗粒，并负载于炭黑。实验结果表明，Ru-Ni/NiO 纳米颗粒尺寸影响着 Ru-Ni/NiO/C 催化剂催化苯加氢制环己烷性能。Ru-Ni/NiO 纳米颗粒平均尺寸为 2~3 nm 左右时，其催化活性最高。

总之，本文研究内容一方面可为根据不同反应设计具有分工协同多活性位的催化剂提供一定的理论依据，且为制备低成本贵金属基催化剂贡献了一种简单的方法（贵金属与过渡金属的复合）；另一方面，进一步理解了双金属催化剂纳米结构与尺寸对催化性能的影响，为更好地设计双金属纳米催化剂提供参考。

关键词：多活性位的分工协同；苯加氢；Ru-Ni/NiO/C 催化剂；Ru-Co/Co_3O_4/C 催化剂；构效关系

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Abstract

The rational design of catalysts is very important to realize effective adsorption and activation of reactants for the enhancement of catalytic activity, selectivity and stability of heterogeneous catalysts. Because most of the catalytic reactions involve two or more reactants, an ideal catalyst should have multiple and synergetic sites that are active towards different reactants. Aromatic compounds are a kind of important compounds and platform chemicals for chemical industries. Their extended products are those of the hydrogenation of aromatic ring. Take the hydrogenation of benzene as an instance. Benzene hydrogenation can produce cyclohexane, which is a significant chemical intermediate mainly used for the manufacture of cyclohexanol, cyclohexanone and caprolactam-the monomer of nylon-66 and the nylon 6, as well as an excellent solvent in organic chemical industry. Therefore, it is primarily important to design and develop a highly efficient and low-cost catalyst for aromatic hydrogenation reaction. Meanwhile, some universal findings on hydrogenation catalysts could be concluded from this study, which is of particular value in academic research and industrial application.

In this study, the first part is to design and prepare the Ru-Ni/NiO/C catalyst-noble metal Ru islands loaded on Ni/NiO nanoparticles (NPs) and then supported on carbon black. This catalyst has synergetic multiple catalytic sites (Ru, Ni and NiO sites), showing high performance in aromatic hydrogenation reaction. Such a philosophy is evolved to successfully prepare Ru-Co/Co_3O_4/C hydrogenation catalyst, with much higher catalytic activity than Ru-Ni/NiO/C. Due to the synergy of two metals, bimetallic nanomaterials take on new physical and chemical properties, attracting considerable attention to their controllable preparation and application. And the bimetallic nanocatalysts have been widely applied in heterogeneous catalysis. The parameters such as nanostructure, size and composition of bimetallic nanocatalysts highly influence their catalytic properties, selectivity and stability. Therefore, in the

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second part of this study, benzene hydrogenation to cyclohexane is taken as a model reaction and RuNi/C as catalyst, to investigate the intrinsic relationship between the catalytic activity in benzene hydrogenation to cyclohexane and the nanostructure and size of RuNi bimetallic nanoparticles (BNPs).

The main research results obtained in this work are as follows:

1. Here, we report a new approach to design and prepare catalysts with multiple active sites by demonstrating a novel combination of noble metal and transition metal oxide. This approach is exemplified by the design of the Ru-Ni/NiO/C catalyst. Taking the hydrogenation of benzene to cyclohexane as a model reaction, the catalytic activity of Ru-Ni/NiO/C for benzene hydrogenation is found to be 55 times higher than Ru-Ni nanoalloy or Ru supported on Ni NPs (Ru-Ni/C) and 10~11 times higher than the conventional Ru/C. And the difference in the nanostructure and atomic scale of the Ru-Ni/NiO and Ru-Ni NPs are characterized by thermal-gravity (TG), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscope (TEM), high resolution transmission electron microscope (HRTEM), aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (Cs-HAADF-STEM), energy dispersive X-ray spectroscopy elemental mapping (EDS-mapping) and line-scan, high-sensitivity low-energy ion scattering spectroscopy (HS-LEIS), X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure spectroscopy (EXAFS). The research results indicate that the high activity of the Ru-Ni/NiO/C catalyst is attributed to the synergetic multiple catalytic sites, where Ru sites activate molecular hydrogen, NiO sites activate benzene, and Ni sites function as a "bridge" for transferring activated H species to activated benzene by hydrogen spillover.

2. In order to further prove the concept of designing the synergetic multiple catalytic sites, herein, a simple hydrazine hydrate reduction was adopted for the synthesis of $Co/Co(OH)_2/C$, and $Ru-Co/Co(OH)_2/C$ was obtained by galvanic replacement reaction. The $Ru-Co/Co_3O_4/C$ and Ru-Co/C catalysts were gained after $Ru-Co/Co(OH)_2/C$ calcined in N_2 or N_2+H_2 at 280 ℃ for 3 h, respectively. A series of characterizations verify that the $Ru-Co/Co_3O_4/C$ catalyst contains Ru islands

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supported on Co/Co_3O_4 NPs and Ru-Co/C is mainly present in the form of Ru-Co nanoalloy. And the experimental results of benzene hydrogenation to cyclohexane show that the $Ru\text{-}Co/Co_3O_4/C$ catalyst exhibits the most excellent catalytic property in benzene hydrogenation to cyclohexane, much higher than the Ru-Co/C or Ru/C catalyst. Additionally, the catalytic performance of the $Ru\text{-}Co/Co_3O_4/C$ catalyst for benzene hydrogenation is 5 times higher than Ru-Ni/NiO/C. This is primarily attributed to the strong synergetic effect-specialization and cooperation of Ru (activate H_2), Co_3O_4 (activate benzene) and Co sites (as a "bridge" for transferring activated H species via hydrogen spillover). Also, the Ru-Co bimetallic nanostructures are successfully modulated by adjusting the thermal treatment conditions. Therefore, this study provides theoretical foundation for the design and synthesis of low-cost and highly-active catalysts for the hydrogenation of aromatics.

3. The intrinsic relationship between the thermal treatment conditions in N_2 and their catalytic performance in the hydrogenation of benzene to cyclohexane has been established. Firstly, the $Ru\text{-}Ni/Ni(OH)_2/C$ catalysts are prepared at room temperature (RT) via hydrazine hydrate reduction and galvanic replacement methods; secondly, the RuNi bimetallic nanostructures, chemical states of Ru and Ni are successfully modulated by altering thermal treatment temperature in N_2 (uncalcinated, 160 ℃, 230 ℃, 280 ℃, 380 ℃, 480 ℃, 580 ℃ and 680 ℃). The characterizations results of XRD, XPS, TEM, HRTEM, HAADF-STEM, EDS-elemental mapping, line-scan and HS-LEIS analysis indicate that: when $Ru\text{-}Ni/Ni(OH)_2/C$ annealed at below 380 ℃, the main Ru species is Ru(0) while Ni is in the form of oxidation state, nanostructure -Ru islands supported on Ni/NiO (or $Ni/Ni(OH)_2$) NPs; 480 ℃-the main Ru and Ni species is RuO_2 and NiO, respectively, nanostructure-RuO_2 NPs loaded on NiO NPs; above 580 ℃-the main Ru and Ni species is Ru(0) and Ni(0), respectively, nanostructure-Ru@thin Ni core-shell. Finally, the relationship of the thermal treatment conditions-catalytic properties in benzene hydrogenation to cyclohexane is established. The catalytic performance of Ru-Ni/NiO/C-380 ℃ is about 3~4 times higher than that of Ru@thin Ni/C-above 580 ℃, while $RuO_2/NiO/C$-480 ℃ is not active in this reaction.

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4. To achieve aimed catalytic performance, bimetallic catalysts with specific nanostructure should be designed and synthesized. Herein, the $Ru_{0.04}Ni_{0.96}$/C ~uncalcined catalysts (Ru/Ni atomic ratio = 0.04/0.96) are also synthesized by the preparation methods of "2" and "3". The $Ru_{0.04}Ni_{0.96}$ BNPs with different nanostructures (Ru-Ni nanoalloy-230 ℃ or 280 ℃, Ru@thick Ni-480 ℃ and Ru islands-on-Ni particles-680 ℃) are gained after annealed in flowing N_2+H_2 at different temperatures. And the various nanostructures of $Ru_{0.04}Ni_{0.96}$ BNPs have been proved by kinds of characterizations. Their catalytic activity is evaluated using benzene hydrogenation reaction. The relationship between the nanostructure of $Ru_{0.04}Ni_{0.96}$ BNPs and their catalytic performance for benzene hydrogenation reaction is presented in this work. It is found that Ru-Ni nanoalloy/C and Ru islands-on-Ni particles/C are much more active than Ru@thick Ni/C. This finding provides a simple method to design and control the nanostructures of BNPs.

5. Ru-Ni/NiO BNPs with various mean sizes supported on carbon black have been prepared via hydrothermal synthesis at various temperatures and galvanic replacement methods. This study shows that the catalytic benzene hydrogenation to cyclohexane performance of the Ru-Ni/NiO/C catalysts highly depends on the mean size of Ru-Ni/NiO BNPs. The optimum mean size for the highest catalytic activity was proved to be around 2~3 nm.

In conclusion, on one hand, this work provides a theoretical basis for designing a catalyst with synergetic multiple catalytic sites according to different reactions, and furnishes a simple method for the preparation of a low-cost noble metal based catalyst (combination of noble and transition metal); on the other hand, we further understand the factors determining catalytic properties of bimetallic catalysts (nanostructure and size), which could be served as a reference for designing the bimetallic nanocatalysts .

Key Words: Synergetic multiple catalytic sites; benzene hydrogenation; Ru-Ni/NiO/C catalyst; Ru-Co/Co_3O_4/C catalyst; relationship of nanostructure-activity

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