柠檬酸络合法制备 Ba 促进 ZrO₂ 负载 Ru 催化剂上氨合成反应性能

林建新*, 王自庆, 张留明, 倪 军, 王 榕, 魏可镁

福州大学化肥催化剂国家工程研究中心, 福建福州 350002

摘要: 采用柠檬酸络合法制备了一系列不同含量 Ba 掺杂的 ZrO₂, 再用浸渍法制备了 K-Ru/Ba-ZrO₂ 催化剂并将其用于氨合成反应. 采用 X 射线衍射和 CO₂ 程序升温脱附技术考察了 Ba 含量对催化剂结构与性能的影响. 结果表明, Ba 掺入 ZrO₂ 后形成的 BaZrO₃ 有助于其负载的 Ru 催化剂氨合成活性的显著提高. 在 5.0 MPa, 10000 h⁻¹, 425 °C 时, Ru/Ba-ZrO₂ (Ba:Zr 摩尔比为 1:1) 催化剂活性最高, 出口氨浓度和反应速率分别达 9.24% 和 29.77 mmol/(g·h). 这主要归因于载体的强电子传导性能和碱性提高.

关键词: 钡; 二氧化锆; 钌; 氨合成; 电子作用

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*通讯联系人. 电话: (0591)83731234-8102; 电子信箱: lin3jx@fzu.edu.cn

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Ammonia Synthesis over Ruthenium Catalysts using Barium-Doped Zirconia as Supports Prepared by Citric Acid Method

LIN Jianxin*, WANG Ziqing, ZHANG Liuming, NI Jun, WANG Rong, WEI Kemei

National Engineering Research Center of Chemical Fertilizer Catalyst, Fuzhou University, Fuzhou 350002, Fujian, China

Abstract: Barium-promoted zirconia (Ba-ZrO₂) was synthesized by the citric acid method and used as supports for Ru/Ba-ZrO₂ catalysts, which were prepared by incipient wetness impregnation with K₂RuO₄ as precursor. The obtained Ba-ZrO₂ and catalysts were characterized by X-ray diffraction and CO₂ temperature-programmed desorption. The effect of Ba content on the structure and catalytic activity of K-Ru/Ba-ZrO₂ catalysts is discussed. The formation of BaZrO₃ can improve significantly the catalytic activity of Ru/Ba-ZrO₂ for ammonia synthesis. The ammonia concentration and rate of ammonia synthesis of the K-Ru/Ba-ZrO₂ catalyst (molar ratio of Ba:Zr is 1:1) were 9.24% and 29.77 mmol/(g·h), respectively, at 425 °C, 5.0 MPa, and 10000 h⁻¹. Improvements in electron conductivity and the basic nature of the catalyst may be the main reasons for such high catalytic activity in ammonia synthesis.

Key words: barium; zirconia; ruthenium; ammonia synthesis; electronic conductivity

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*Corresponding author. Tel: +86-591-83731234-8102; E-mail: lin3jx@fzu.edu.cn

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继铁催化剂之后的第二代 Ru 基催化剂在温和条件下就具有较高的氨合成活性, 因此成为氨合成催化剂研究的一个重要方向. 其中, 石墨化活性炭材料负载钌氨合成催化剂早在上世纪 90 年代就已

经实现工业化^[1,2]. 然而, 该催化剂存在明显的甲烷化反应, 因此以高稳定性金属氧化物负载钌制备出一种高活性的钌基氨合成催化剂成为该领域的一个研究热点. 目前, 研究较多的氧化物主要有 MgO,

Al_2O_3 ^[3-5]、稀土氧化物及其复合氧化物^[6,7]。 ZrO_2 是一种颇具特色的多功能纳米材料,是唯一同时具有酸性、碱性、氧化性和还原性的金属氧化物^[8],其内部和表面容易产生氧空位,能与活性组分产生较强的相互作用,具有良好的结构稳定性,但酸性位的存在限制了它在氨合成和氨分解催化反应中的应用^[9]。随着纳米材料制备技术的发展,功能化纳米 ZrO_2 材料开始大量应用于催化反应^[10,11],有关将 Ba 掺杂 ZrO_2 作为载体用于钌基氨合成催化剂尚未见报道。

采用柠檬酸络合法制备催化剂载体。将一定量的 $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ 和 $\text{Ba}(\text{NO}_3)_2$ 溶于适量的蒸馏水,得到无色澄清溶液。在强烈搅拌作用下,将摩尔比为 1:3 的柠檬酸的乙二醇溶液缓缓倒入上述澄清溶液中。将该混合溶液置于 90 °C 水浴中加热直到得到黄色凝胶,然后在 300 °C 焙烧 3 h,在 780 °C 焙烧 5 h 即可得到 Ba 掺杂的 ZrO_2 样品,记为 Ba- ZrO_2 -X (X 为 Ba/Zr 的摩尔比)。将 K_2RuO_4 溶液多次浸渍到上述载体中。采用无水乙醇还原后,于红外灯下干燥 4 h,即得催化剂 K-Ru/Ba- ZrO_2 -X。所有样品中 Ru 的含量均为 4%。

氨合成反应在四槽连续流动反应器中进行,催化剂 (12~16 目) 装量 2 ml。测试前催化剂在常压下用反应气 ($\text{H}_2/\text{N}_2 = 3:1$) 分别于 200, 300, 400, 425, 450 和 475 °C 活化 2 h,然后在 5 MPa,空速为 10000 h^{-1} 条件下稳定 2 h,产物氨气用标准浓度稀硫酸吸收,根据硫酸当量、吸收时间和剩余氢氮气体积计算出口反应气中氨的浓度。

X 射线衍射 (XRD) 测试在荷兰 PANalytical 公司 X'Pert Pro 型粉末衍射仪上进行,采用 $\text{Co K}\alpha$ 射线,管电压 40 kV,管电流 40 mA,扫描范围 $2\theta = 10^\circ \sim 90^\circ$ 。 CO_2 程序升温脱附测试在 Micromeritics 公司 AutoChem 2910 型全自动催化剂表征系统上进行,测试程序同文献[5],样品的用量为 60 mg。

表 1 是不同量 Ba 掺杂 ZrO_2 负载的 Ru 催化剂上氨合成反应活性。可以看出,催化剂活性随着 Ba 含量的升高而不断提高,当 Ba 与 Zr 的摩尔比为 1.0 时,达到最大值。样品 K-Ru/Ba- ZrO_2 -1.0 于 425 °C 时出口氨浓度和反应速率分别为 9.24% 和 29.77 $\text{mmol}/(\text{g} \cdot \text{h})$,远大于文献报道的 10.0 MPa 时,相同温度下 Ru/Sm- Al_2O_3 ^[3-5], Ru/La $_2\text{O}_3$ ^[6], Ru/Sm $_2\text{O}_3$ ^[7] 和 Ba-Ru/NB^[12] 等的催化活性。继续增加 Ba 含量,催化剂活性降低。

图 1 为各 Ba- ZrO_2 样品的 XRD 谱。由图可见,各样品均出现立方晶相 BaZrO_3 ($2\theta = 35.32^\circ, 43.48^\circ, 50.73^\circ, 63.43^\circ, 74.45^\circ, 85.33^\circ$) 的特征衍射峰。其强度随着 Ba 含量的增加而增强,当 Ba 与 Zr 的摩尔比小于 1.0 时,载体还有 ZrO_2 的特征衍射峰,其强度随着 Ba 含量的增加而下降。当 Ba 与 Zr 的摩尔比为 1.2 时,载体中出现较明显的 BaCO_3 ($2\theta = 27.92^\circ$) 的特征衍射峰。钙钛矿型 BaZrO_3 具有丰富

图 1 不同 Ba- ZrO_2 样品的 XRD 谱
Fig. 1. XRD patterns for various Ba- ZrO_2 samples. (1) Ba- ZrO_2 -0.10; (2) Ba- ZrO_2 -0.50; (3) Ba- ZrO_2 -1.0; (4) Ba- ZrO_2 -1.2.

表 1 Ba 促进 ZrO_2 负载 Ru 催化剂上氨合成反应性能

Table 1 The ammonia synthesis properties of different K-Ru/Ba- ZrO_2 catalyst samples

Catalyst	NH_3 concentration (%)			$r/(\text{mmol}/(\text{g} \cdot \text{h}))$		
	400 °C	425 °C	400 °C	400 °C	425 °C	450 °C
K-Ru/Ba- ZrO_2 -0.1	4.06	7.10	7.97	11.81	21.32	24.17
K-Ru/Ba- ZrO_2 -0.5	5.42	8.54	8.79	16.00	26.05	26.89
K-Ru/Ba- ZrO_2 -1.0	7.56	9.24	9.17	22.82	29.77	29.53
K-Ru/Ba- ZrO_2 -1.2	5.57	7.28	6.18	12.56	18.98	21.32

Reaction conditions: 5.0 MPa, 10000 h^{-1} .

的氧晶格缺陷和较强的碱性位^[13], 同时又是一种性能优良的固体电解质, 具备优良的电子导电性^[14]. 大量研究已经证明^[15~18], 载体的电子传导性能是决定 Ru 基氨合成催化剂性能的主要因素. 因此, 在 ZrO_2 表面生成的 BaZrO_3 使载体的电子传导性能增强, 从而提高了催化剂的活性. BaCO_3 物相的生成可能降低了载体的电子传导能力, 导致 Ba 与 Zr 的摩尔比大于 1.0 时催化剂活性反而降低.

研究表明^[15,19,20], Ru 基氨合成催化剂活性与载体表面酸碱性能密切相关, 即碱性载体有利于氨合成反应的进行. 因此, 本文采用 CO_2 -TPD 测试了催化剂表面碱性位的数量和强度, 结果见图 2. 可以看出, 在测试温度范围内, 在 50~150 °C 和 450~750 °C 存在两个明显的 CO_2 脱附峰, 表明载体表面存在两种强度和数量均不同的碱性位. 虽然随着 Ba 含量的增加材料表面碱性的强度在不断降低, 但其数量却明显增加. Ba-ZrO₂-1.2 的碱性大于 Ba-ZrO₂-1.0, 但其负载的 Ru 催化剂活性却明显下降, 这可能是由于 BaCO_3 的生成降低了载体的电子传导能力所致.

图 2 不同 Ba-ZrO₂ 样品的 CO_2 -TPD 谱

Fig. 2. CO_2 -TPD profiles of various Ba-ZrO₂ with different contents of Ba. (1) Ba-ZrO₂-0.10; (2) Ba-ZrO₂-0.50; (3) Ba-ZrO₂-1.0; (4) Ba-ZrO₂-1.2.

综上所述, 采用柠檬酸络合法制备的 Ba 促进 ZrO_2 负载的 Ru 具有优异的低温低压氨合成活性. 在柠檬酸燃烧过程中瞬时高温的作用下, 掺杂的 Ba 部分进入 ZrO_2 晶格形成了钙钛矿型 BaZrO_3 ^[21], 有助于将电子助剂钾提供的电子和自身电子传递到金属 Ru 粒子的表面, 从而促进了 $\text{N}\equiv\text{N}$ 的断裂^[22,23].

催化剂活性的提高还可能与载体的碱性有关. 有关该催化剂的其它性能和提高氨合成活性的研究正在进行中.

参 考 文 献

- Niwa Y, Aika K. *J Catal*, 1996, **162**: 138
- Rossetti I, Mangiarini F, Forni L. *Appl Catal A*, 2007, **323**: 219
- Lin B Y, Wang R, Lin J X, Du S W, Yu X J, Wei K M. *Catal Commun*, 2007, **8**: 1838
- Lin B Y, Wang R, Lin J X, Ni J, Wei K M. *Catal Commun*, 2011, **12**: 553
- 张新波, 李小年, 霍超, 岑亚青, 祝一锋, 刘化章. 催化学报 (Zhang X B, Li X N, Huo Ch, Cen Y Q, Zhu Y F, Liu H Zh. *Chin J Catal*), 2002, **23**: 207
- Luo X J, Wang R, Ni J, Lin J X, Lin B Y, Xu X M, Wei K M. *Catal Lett*, 2009, **133**: 382
- Zhang L M, Lin J X, Ni J, Wang R, Wei K M. *Catal Commun*, 2011, **15**: 23
- Tanabe K. *Mater Chem Phys*, 1985, **13**: 347
- Yin Sh F, Xu B Q, Wang Sh J, Au Ch K. *Appl Catal A*, 2006, **301**: 202
- Sun G L, Xu A H, He Y, Yang M, Du H Zh, Sun Ch L. *J Hazard Mater*, 2008, **156**: 335
- 刘仲毅, 孙海杰, 王栋斌, 郭伟, 周小莉, 刘寿长, 李中军. 催化学报 (Liu Zh Y, Sun H J, Wang D B, Guo W, Zhou X L, Liu Sh Ch, Li Zh J. *Chin J Catal*), 2010, **31**: 150
- 徐春风, 欧阳亮, 张佳, 周斌, 李瑛, 刘化章. 催化学报 (Xu Ch F, Ouyang L, Zhang J, Zhou B, Li Y, Liu H Zh. *Chin J Catal*), 2010, **31**: 677
- Li X C, Wu M, Lai Zh H, He F. *Appl Catal A*, 2005, **290**: 81
- Takeuchi K, Loong C K, Richardson J W Jr, Guan J, Dorris S E, Balachandran U. *Solid State Ionics*, 2000, **138**: 63
- You Z X, Inazu K, Aika K, Baba T. *J Catal*, 2007, **251**: 321
- Aika K, Tamaru K. In: Nielsen A Ed. *Ammonia: Catalysis and Manufacture*. Berlin: Springer-Verlag, 1995. 103
- Liang Ch H, Li Z L, Qiu J S, Li C. *J Catal*, 2002, **211**: 278
- 高伟洁, 郭静淑, 张洪波, 潘秀莲, 包信和. 催化学报 (Gao W J, Guo J Sh, Zhang H B, Pan X L, Bao X H. *Chin J Catal*), 2011, **32**: 1418
- Song Z, Cai T, Hanson J C, Rodriguez J A, Hrbek J. *J Am Chem Soc*, 2004, **126**: 8576
- 杨晓龙, 唐立平, 夏春谷, 熊绪茂, 慕新元, 胡斌. 催化学报 (Yang X L, Tang L P, Xia Ch G, Xiong X M, Mu X Y, Hu B. *Chin J Catal*), 2012, **33**: 447
- Sin A, E Montaser B, Odier P. *J Sol-Gel Sci Technol*, 2003, **26**: 541
- 罗小军, 王榕, 林建新, 魏可镁. 催化学报 (Luo X J, Wang R, Lin J X, Wei K M. *Chin J Catal*), 2009, **30**: 1125
- Saito M, Itoh M, Iwamoto J, Li Ch Y, Machida K. *Catal Lett*, 2006, **106**: 107

英 译 文 English Text

Ru-based catalysts are considered to be second-generation catalysts for ammonia synthesis since they exhibit remarkably high activity compared to conventional Fe-based catalysts, especially at low temperature and pressure. Carbon-supported Ru catalysts have been used for industrial ammonia synthesis since the 1990s [1,2]. To overcome the significant drawback of using activated carbon supports which are prone to methanation under the temperatures and pressures required for ammonia synthesis, many stable metal oxides, such as MgO, Al₂O₃ [3–5], rare earth oxides and their mixture compounds [6,7] were studied with the aim of preparing a Ru-based catalyst with high activity. ZrO₂ is a versatile material and is the only metal oxide which can act as both acid and base, oxidant or reductant [8]. It has been used widely as a catalyst and catalyst support. Unfortunately, there are few reports involving the application of ZrO₂ in ammonia synthesis or decomposition, owing to its acidity [9]. With the development of research into the preparation of nanoparticles, the application of modified ZrO₂ has been reported widely [10,11]. To our knowledge, there has been no previous report on the barium-modified ZrO₂ as the support for the Ru-based catalyst for ammonia synthesis.

A series of barium-modified ZrO₂ materials were prepared by combustion of the citrate sol-gel process. First, a certain amount of analytical-grade Zr(NO₃)₄·5H₂O and Ba(NO₃)₂ was dissolved in deionized water to form a transparent mixed nitrate solution. The citric acid monohydrate was dissolved in diethylene glycol under continuous stirring at the molar ratio of 1:3. The citric acid solution was added slowly to the mixed nitrate solution and a transparent solution resulted. The solution was then evaporated using a water bath at 90 °C to promote gelation until a yellow gel was obtained. The gel was maintained at 300 °C for 3 h to obtain the precursor and then calcined at 780 °C for 5 h. The resultant white powder was denoted Ba-ZrO₂-*X*, where *X* is the molar ratio of Ba to Zr. Ruthenium catalysts were prepared by impregnating the supports directly with K₂RuO₄ solution. After reduction with ethyl alcohol, they were dried under the infrared lamp for 4 h. The samples with 4 wt% Ru were labeled as K-Ru/Ba-ZrO₂-*X*.

The catalyst activity for ammonia synthesis was measured in a stainless steel reactor. Before testing, the catalysts were activated in a flowing gas mixture of 75% H₂ and 25% N₂ from ambient temperature to 475 °C at 1 °C/min (maintained at 200, 300, 450, and 475 °C for 2 h each) and then stabilized at the reaction conditions (i.e. 5 MPa, 400 °C, 10000 h⁻¹, and H₂:N₂ volume ratio of 3) for more than 2 h. The ammonia

concentration in the effluent was determined by a chemical titration method.

X-ray diffraction (XRD) analysis was carried out on an Analytical X'Pert Pro diffractometer system, using Co *K*_α radiation (0.1789 nm). CO₂ temperature-programmed desorption (CO₂-TPD) was determined according to Ref. [5] (all samples weighed 60 mg).

The catalytic activity of K-Ru/Ba-ZrO₂-*X* is given in Table 1. The catalytic activity of the K-Ru/Ba-ZrO₂ catalysts increased with increasing Ba content up to a certain value and then decreased with further Ba loading. K-Ru/Ba-ZrO₂-1.0 showed the highest activity while the highest ammonia concentration and maximum ammonia synthesis rates were 9.24% and 29.77 mmol/(g·h), respectively, at 5 MPa, 425 °C, and 10000 h⁻¹. This activity was much higher than the other catalysts with more or less Ba content and than other previously reported catalysts (such as Ru/Sm-Al₂O₃ [3–5], Ru/La₂O₃ [6], Ru/Sm₂O₃ [7], Ba-Ru/NB [12]), although the latter catalysts' activity was measured at high pressure (10 MPa, 10000 h⁻¹).

The XRD patterns of the Ba-ZrO₂-*X* composites with different Ba:Zr molar ratios are shown in Fig. 1. One can see that Ba-ZrO₂-0.10 and Ba-ZrO₂-0.50 show clear peaks attributable to ZrO₂ and barium zirconate (BaZrO₃). The formation of orthorhombic barium carbonates is only observed for Ba-ZrO₂-1.2. BaZrO₃ with ideal perovskite structure is an alkaline material and solid-electrolyte with abundant oxygen vacancies, which exhibit high proton and electronic conductivity [13,14]. Many papers have proven that the effectiveness of a support for ammonia synthesis is related approximately to the basic nature and electrical conductivity of the compound [15–18]. The presence of BaZrO₃ on the ZrO₂ surface could therefore promote the electrical conductivity of the supports and transmit the electrons of K promoters to the Ru surface directly, thereby increasing the Ru catalyst activity significantly. However, the presence of BaCO₃ in the Ba-ZrO₂-1.2 would decrease the electrical conductivity and may be the main reason for the poor performance of K-Ru/Ba-ZrO₂-1.2.

Many papers have proven that the strong basicity of support materials is conducive to the activity of Ru-based catalysts for ammonia synthesis and that the stronger the support basicity, the higher the catalytic performance [15,19,20]. CO₂-TPD was carried out to measure the amount and strength of the basic sites on the catalyst surface and the results are shown in Fig. 2. It is obvious that the CO₂-TPD of all the samples contained two partially separated desorption peaks, indicating that a variety of basic sites with different strengths were present on the surface. The peak appearing at 50–150 °C could be ascribed to the weak basic site, while the high temperature peak resulted from the strong basic site. The phenomenon where the basic site strength is weakened

with increase in Ba content in the support is also observed. However, the number of basic sites increases, which increases the activity for ammonia synthesis. The catalytic activity of K-Ru/Ba- ZrO_2 -1.2 is lower than that of K-Ru/Ba- ZrO_2 -1.0 although the number of basic sites is in contrast, which may be responsible for the presence of BaCO_3 because the formation of BaCO_3 could cover the basic site on the surface of BaZrO_3 .

In conclusion, the series of Ba-doping ZrO_2 materials prepared by the citric acid method supported Ru catalysts all displayed excellent catalytic activity for ammonia synthesis

at low temperature and pressure. The phenomenon may result from the formation of BaZrO_3 in the supports at high temperature, which would increase electron conductivity and basicity. Mobile electrons donated from the promoter K and BaZrO_3 itself to the Ru metal particles facilitated the cleavage of $\text{N}\equiv\text{N}$ by the solid electrolyte support, BaZrO_3 . Further improvements in the ammonia synthesis properties and structure-effect relationship are being investigated.

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