

改性ZrO₂负载钌氨合成催化剂的制备及其构效关系研究

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Ammonia synthesis over ruthenium supported on modified zirconia: Relationships between the catalyst structure and activity

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摘要 由ZrO(NO₃)₂水解得到的ZrO(OH)₂水凝胶经碱液回流老化、焙烧后制备了改性ZrO₂载体材料,直接浸渍K₂RuO₄溶液,经还原后用于催化氨合成反应。并运用X射线衍射(XRD)、CO₂程序升温脱附(CO₂-TPD)、X射线荧光光谱(XRF)、N₂物理吸附、H₂程序升温还原技术(H₂-TPR)和CO化学吸附对其进行了表征,重点考察了催化剂性能与载体性能间的构效关系。结果表明,KOH和NH₄OH溶液回流均可提高载体的比表面积,但是KOH回流制备的载体同时还具有较强的碱性,因此,负载钌以后表现出最佳活性。在425 °C、5 MPa、空速为10 000 h⁻¹条件下,出口氨浓度为5.96%,分别较催化剂K-Ru/ZrO₂-NH₄OH、K-Ru/ZrO₂-CP和Ru/ZrO₂-NH₄OH提高了11%、143%和103%。与活性组分分散度相比,载体碱性强度对活性的促进作用更为明显。

关键词: 碱液回流 二氧化锆 钌 氨合成 碱性

Abstract: Modified zirconia (ZrO₂) were synthesized by high temperature calcination of ZrO(OH)₂ gels digested in alkalic solution; with the modified ZrO₂ as support, ruthenium catalysts for ammonia synthesis were prepared with K₂RuO₄ solution. The catalysts were characterized by X-ray diffraction (XRD), temperature programmed reduction of hydrogen (H₂-TPR), temperature programmed desorption of CO₂ (CO₂-TPD), nitrogen sorption, X-ray fluorescence spectroscopy (XRF), and CO chemisorption; the relationship between the catalyst structure and its catalytic activity was especially discussed. The results revealed that the digestion either in KOH or NH₄OH solution can enhance the surface area of the ZrO₂ support, while digestion in KOH is able to obtain the support with high basicity, which benefits to getting the ruthenium catalyst of high activity. The strong basicity of the modified ZrO₂ support, rather than the high ruthenium dispersion, plays a more important role in enhancing the activity of the supported ruthenium catalyst. For ammonia synthesis under 425 °C, 5 MPa and a space velocity of 10 000 h⁻¹, NH₃ outlet concentration over Ru/ZrO₂-KOH is 5.96%, which is 11%, 143% and 103% higher than those of K-Ru/ZrO₂-NH₄OH, K-Ru/ZrO₂-CP and Ru/ZrO₂-NH₄OH, respectively.

Key words: digestion in basic solution zirconia ruthenium ammonia synthesis basicity

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