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P 对 Cu/Al_2O_3 催化剂结构及其催化甘油氢解反应性能的影响

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摘要 采用分步浸渍法制备了 P 改性的 Cu/Al_2O_3 催化剂, 利用 N2 吸附-脱附、X 射线衍射、红外光谱、紫外-可见光谱、H2 程序升温还原、NH3 程序升温脱附和 N_2O 解离吸附等方法对催化剂进行了表征, 考察了 P 含量及浸渍次序对催化剂结构及其催化甘油氢解反应性能的影响. 结果表明, 先浸渍 P 再浸渍 Cu 时, 所制 Cu/Al_2O_3 催化剂酸性较高, 同时还促进了 Cu 的分散. 随 P 含量的增加, 催化剂的酸量及 Cu 分散度提高, 并且 Cu 与 P 物种的相互作用增强; 然而, P 含量较高时会覆盖 Cu, 使暴露的 Cu 表面降低. 先浸渍 Cu 后浸渍 P 时, 尽管也提高了相应催化剂的酸性, 但对 Cu 分散的影响不大, 并且还会覆盖 Cu 使暴露的 Cu 表面明显降低. 先浸渍 P 明显提高了 Cu/Al_2O_3 上甘油氢解反应性能. 在 220 ºC, 3 MPa, 质量空速 2 h^{-1}以及 H2/甘油摩尔比 20 的条件下, 当 P 含量由 0 增加至 6% 时, 甘油转化率从 17.1% 升至 95.0%, 1,2-丙二醇选择性从 83.7% 升至 97.2%. 这可归因于催化剂酸性的提高及 Cu 与 P 间的相互作用.

关键词: 甘油氢解 铜基催化剂 磷 甘油 1,2-丙二醇 酸性 分散度

Abstract: Phosphorus (P) modified Cu/Al_2O_3 catalyst was prepared by the successive impregnation method. The physicochemical properties of the catalyst were studied by means of N_2 adsorption-desorption, X-ray diffraction, infrared spectroscopy, UV-visible diffuse reflectance spectroscopy, H_2 temperature-programmed reduction, NH_3 temperature-programmed desorption, and dissociative N_2O adsorption. The effects of the P content and the impregnation sequence on the structure and the performance of the catalyst for the hydrogenolysis of glycerol to 1,2-propanediol (1,2-PDO) were discussed. The addition of P to Cu/Al_2O_3 enhanced the acidity and Cu dispersion, especially when P species was impregnated prior to Cu. Also, there was a strong interaction between P and Cu species. However, the strong interaction leads to the coverage of Cu atoms with the P species at high P content. The coverage may be more serious when the P species was added after Cu to the catalyst. In the hydrogenolysis of glycerol, the addition of P prior to Cu remarkably promoted the catalytic performance of Cu/Al_2O_3. Under the conditions of 220 ºC, 3.0 MPa, space velocity of 2.0 h^{-1}, and the H_2/glycerol molar ratio of 20, as the P content increased from 0 to 6%, the glycerol conversion and the 1,2-PDO selectivity increased from 17.1% to 95.0% and from 83.7% to 97.2%, respectively. The promotion effect of P on the performance of Cu/Al_2O_3 is attributed to the increase of catalyst acidity as well as the strong interaction between Cu and P species.

Keywords: glycerol, hydrogenolysis, copper-based catalyst, phosphorus, glycerol, 1,2-propanediol, acidity, dispersion

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