Rh 掺杂改性 Cu 基催化剂上甲烷-合成气两步法合成乙醇：掺杂比例的影响

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乙醇作为优质、清洁能源，具有广泛的应用前景。Rh基催化剂上合成气合成乙醇是目前的研究热点 [1]。但是，Rh基催化剂上合成气合成乙醇反应中，CH_4的生成影响了乙醇的产率和选择性，而且Rh催化剂价格昂贵限制了其工业化应用。通过在合成气中引入CH_4 [2]，本实验室提出采用全新反应机理的甲烷-合成气合成乙醇工艺路线，不仅可以解决合成气合成乙醇反应中CH_x的来源问题，同时能够有效抑制合成气转化中甲烷的生成。通过采用密度泛函理论(DFT)研究了不同比例Rh掺杂改性的RhCu催化剂上，催化剂表面Rh含量对甲烷-合成气两步法合成乙醇反应催化性能的影响，结果表明：适量Rh掺杂改性的Cu基催化剂能够明显提高生成乙醇的选择性和产率，并且计算获得最佳的Rh/Cu比为1/2，该反应中仅伴有少量甲醇和乙烷的生成。甲烷-合成气合成乙醇的反应机理为：首先CH_4直接解离生成CH_3，随后CO插入稳定的CH_x中间体CH_3生成C_2氧化物CH_3CO，最后C_2氧化物连续加氢经CH_3COH，CH_3CHOH中间体生成乙醇。

关键词： Cu基催化剂；甲烷-合成气；乙醇；密度泛函理论

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The Formation Mechanism of Ethanol from Methane-syngas over Rh-Doped Cu Catalysts: Insight into the Effect of Dope Ratio

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Ethanol as a high quality and clean energy has a good application foreground. Ethanol formation from syngas on Rh-based catalysts is the research center and development direction at present. However, the commercial utilization is limited by the high cost of Rh catalyst, as well as the yield and selectivity of ethanol affected by the generation of CH_4. It is note that the introduction of CH_4 into the syngas can not only solve the problem of CH_x source, but also inhibit the formation of methane during the conversion of syngas. In this work, ethanol synthesis from methane-syngas via the two-step reaction has been studied over the cheap Cu catalyst doped by the quantitative Rh atoms using DFT calculations. The results show that Rh-doped Cu catalysts can obviously enhance the selectivity toward the production of ethanol, and the optimum Rh/Cu ratio is 1/2. The formation mechanism of ethanol is that: methane directly dissociates to CH_3, then, CH_3 as the most stable CH_x intermediate reacts with CO to produce CH_3CO, followed by the successive hydrogenation to ethanol.

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