论文

Co-Pd催化剂上CH_4/CO_2合成乙酸反应中CO_2与表面金属物种作用的密度泛函理论研究

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摘要：

采用广义梯度近似(GGA)的密度泛函理论(DFT)(DFT-GGA)对Co-Pd催化剂上CH_4/CO_2两步法合成乙酸反应中CO_2与金属表面物种M—H(M=Co,Pd)和Pd—CH_3的插入反应机理进行了研究, 给出了CO_2与M—H和Pd—CH_3的插入反应机理. 计算结果表明, 在CO_2与M—H和Pd—CH_3相互作用的4个反应路径中, 反应以CO_2与Co—H作用生成产物HCOO—Co为动力学优先路径, 但由于HCOO以双齿形式与金属Co结合, 其结合能较大, 导致HCOO在金属表面不易脱附, 故较难形成甲酸; 反应生成H_3CCOO—Pd产物路径次之, H_3CCOO和Pd之间结合能较小, H_3CCOO容易脱附形成主产物乙酸; 生成H_3COOC—Pd反应为动力学最不利路径, 故甲酸甲酯为动力学禁阻产物; 计算结果与实验结果吻合得很好.

关键词： 二氧化碳; 乙酸; 反应机理; Co; Pd; 密度泛函理论; 广义梯度近似

Density Functional Theory Study on Interaction of CO2 with Metal Surface Carbon Species in Synthesis of Acetic Acid from CH4/CO2 on Co-Pd Catalysts

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Abstract:

The insertion reactions of CO_2 with M—H(M=Co, Pd) and Pd—CH_3 were systematically investigated by the first-principle DFT-GGA calculations. The mechanisms of CO_2 reacting with M—H and Pd—CH_3 were obtained for the direct synthesis of acetic acid from CH_4/CO_2 by a two-step reaction sequence on Co—Pd catalysts. The calculation result showed that the pathway that CO_2 inserts into Co—H bonds forming HCOO—Co was the most advantageous in dynamics for all four designed reaction paths. However, HCOO was linked with Co in bi-dentate form, whose binding energy was very large, so the desorption of HCOO hardly taken place and formic acid was little produced. Meanwhile, the pathway that CO_2 inserts into Pd—CH_3 bonds forming H_3CCOO—Pd was secondly preferential pathway favored in dynamics. The binding energy between H_3CCOO and Pd was small, and desorption of H_3CCOO easily occurred, so the main product was acetic acid. While methyl formate was inhibited by dynamics. The calculated result was in accordance with the experimental facts.

Keywords: Carbon dioxide; Acetic acid; Reaction mechanism; Cobalt; Palladium; Density functional theory; General gradient approtimationry(GGA)

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