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研究论文

Nb^+离子活化甲烷脱氢反应机理密度泛函(DFT)研究

李建辉, 夏文生, 万惠霖

厦门大学化学化工学院化学系, 固体表面物理化学国家重点实验室, 厦门 361005

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摘要 通过DFT-UB3LYP方法, 计算了五重、三重和单重自旋态下的气相Nb^+离子活化甲烷脱氢反应的能量变化, 并对其直接式和插入式反应机理进行了比较, 考察了自旋翻转对反应的影响. 结果表明, 插入式脱氢较直接式有利, CH4上的H转移到Nb^+上形成的中间体$HNbCH^+_3$中, 多重度由五重降为三重, 反应活化能垒显著降低; $HNbCH^+3$可经四中心过渡态转化为$(H_2)NbCH^+_2$, 最后生成三重态的$NbCH^+_2+H_2$. 速控步骤为$(H_2)NbCH^+_2$的脱氢. 此外, 通过对V^+, Nb^+, Ta^+活化甲烷的比较研究了三者活化甲烷的反应活性.

关键词 密度泛函理论（DFT） 甲烷 脱氢 铌

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DFT Studies on Dehydrogenation Mechanism of Methane Activated by Gas-phase Niobium Cations

LI Jian-Hui, XIA Wen-Sheng, WAN Hui-Lin

State Key Laboratory for Physical Chemistry of Solid Surfaces, Department of Chemsitry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

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Abstract Density functional calculations were employed to investigate the quintet, triplet and singlet energies of methane direct- or inserted- dehydrogenation by gas-phase Nb^+ as well as the influence of spin-inversion on the reaction mechanism. The results indicate that the inserted-dehydrogenation mechanism is more favorable than the direct-dehydrogenation. The minimum energy reaction path is thought to be related to the spin flip from $2S+1=5$ to 3, which decreases the activation barrier of methane-dehydrogenation significantly. The formed intermediate $HNbCH^+_3$ is transformed into $(H_2)NbCH^+_2$ *via* a four-centered transition state, and the final product is the triplet $NbCH^+_2+H_2$. The rate determined step of reaction is the dehydrogenation of $(H_2)NbCH^+_2$. In addition, the reactivities of gas-phase group V cations (V^+, Nb^+ and Ta^+) towards the dehydrogenation of methane were also discussed.

Key words DFT; Methane; Dehydrogenation; Nb

通讯作者:
夏文生 wsxia@xmu.edu.cn
作者个人主页: 李建辉; 夏文生; 万惠霖