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左旋葡聚糖热解机理的密度泛函理论研究

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A density functional theory study on the mechanism of levoglucosan pyrolysis

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全文: PDF (2681 KB)　HTML (1 KB)　输出: BibTeX | EndNote (RIS)　背景资料

摘要 采用密度泛函理论B3LYP/6-31++G(d,p)方法,对纤维素热解的主要产物左旋葡聚糖的热解反应机理进行了理论计算分析,设计了四种可能的热解反应途径, 对各种反应的反应物、产物和过渡态的结构进行了能量梯度全优化。计算结果表明,左旋葡聚糖开环成链状中间体时,首先,左旋葡聚糖中的两个半缩醛键C(1)-O(7)和C(6)-O(8)断裂,经过渡态TS_1形成中间体IM_1,同时,C(6)-O(7)结合成键使C(5)-C(6)-O(7)形成环状结构,该反应的能垒较高,为296.53 kJ/mol,然后IM_1经过渡态TS_2转变为中间体IM_2,该反应的能垒为234.09 kJ/mol;对IM_2设计了四条可能的反应路径,反应路径2和3能垒较低,是IM_2最可能的热解反应途径;在反应路径1和4中都包含了脱羰基反应,其反应能垒较高,不易发生。

关键词: 左旋葡聚糖　热解反应　密度泛函理论

Abstract: The pyrolysis mechanism of levoglucosan (one of the major product from cellulose pyrolysis) was investigated by using density functional theory at B3LYP/6-31++G(d,p) level. Four possible reaction pathways were proposed and the geometries of reactant, transition states, intermediates and products for each pathway were fully optimized; the standard thermodynamic and kinetic parameters of each reaction at different temperatures were calculated. The results showed that levoglucosan is converted to intermediate IM_1 via transition state TS_1 with an activation energy of 296.53 kJ/mol by breakage of C(1)-O(7) and C(6)-O(8) hemiacetal linkages and formation of C(5)-C(6)-O(7) circular structure, and then IM_1 is converted to intermediate IM_2 via transition state TS_2 with an activation energy of 234.09 kJ/mol. IM_2 can be further decomposed via four different pathways. Pathways 1 and 4 involve decarbonylation reactions with high energy barriers, and as a result, they are unlikely to occur; on the other side, the energy barriers for the rate-determining steps of pathways 2 and 3 are much lower, which are kinetically favorable and possible the major reaction channels for IM_2 pyrolysis.

Key words: levoglucosan　pyrolytic reaction　density functional theory

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