共聚物配体交替结构与其催化活性关系的理论研究

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摘要　本文采用以ASED-MO(含原子对排斥的EHMO法)为基础的结构自动优化的EHTOPT法及Monte-Carlo法,对甲醇羰基化制乙酸催化剂的共聚物配体交替结构进行了理论研究。计算了AA, AB, BB, BA二聚反应的反应途径, 找出了过渡态, 并确定了反应活化势垒。在假设两反应频率因子相同的前提下, 求出竞聚率, 采用Monte-Carlo法模拟共聚物结构, 计算出共聚物配体中起催化活性的AB交替结构所占比率。比较不同共聚物配体的活性, 并研究了温度及单体配比对共聚物配体交替结构的影响。

关键词　竞聚率　分子结构　共聚物　势垒　二聚作用　交替共聚物　催化活性　配体　反应途径　蒙特卡洛模拟　交替结构　ASED-MO

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Theoretical study of the alternative structure of copolymer ligands and activity comparison of copolymer ligands

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Abstract A theoretical study of the alternative structure of copolymer ligands of catalyst for carbonylation of methanol to acetic acid has been carried out in terms of the ASED-MO method and Monte Carlo method. AA, AB, BB, BA reaction pathways were calculated and energy barriers were determined. Based on the supposition of the preexponent factor of rate constants being equal, the reactivity ratios r_1 and r_2 were obtained. The copolymer structure was simulated and caculate the ratio of active AB segment in the copolymer molecular chains was calculated. The relative activity of copolymer ligand consisted of different two units was compared. The effect of temperature change and the feed ratio x, on the ratio of AB in the molecular chains was also discussed.

Key words REACTIVITY RATIO　MOLECULAR STRUCTURE　COPOLYMERS　POTENTIAL BARRIER　DIMERIZATION　ALTERNATING COPOLYMER　CATALYTIC ACTIVITY　LIGANDS　REACTION PATH　MONTE CARLO SIMULATION

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