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钯(Ⅱ)催化CO/乙烯交替共聚反应机理反应状态下钯/膦配位结构的原位^3^1P NMR研究

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摘要 应用加温加压原位核磁技术, 考察了不同配比的钯/膦催化剂在共聚反应条件下(C2H4/CO=1:1, 2.0MPa)的^3^1P NMR谱。实验表明, 在C2H4/CO共聚反应条件下, DPPP(1, 3-双二苯基膦丙烷)与Pd(OAc)2生成比较稳定的六元环螯合物,没有发现游离DPPP的^3^1P NMR信号。当反应温度高于100℃时, 螯合物即开始分解; 反应温度高于260℃时, 螯合物完全分解。DPPP/Pd(OAc)2=1时, 在反应条件下生成有活性的螯合物(DPPP)Pd(OCOCF3)2; DPPP/Pd(OAc)2>=2时, 在反应条件下生成无活性螯合物(DPPP)2Pd(OCOCF3)2。

关键词 反应机理 共聚 乙烯 一氧化碳 膦 钯 磷31核磁共振谱法

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Mechanism of palladium-catalyzed alternating copolymerization of CO with ethylene: In situ ^3^1P NMR studies on palladium-phosphine coordinate structure under reaction conditions

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Abstract Palladium-phosphine catalyst with different DPPP/Pd(OAc)2 ratio has been studied with in situ ^3^1P NMR spectroscopy under reaction conditions (C2H4/CO 1:1, 2.0MPA). The results showed that the reaction of DPPP with Pd(OAc)2 produced a stable six-membered ring complex which had efficient catalytic activity. When the reaction temperature was above 100℃, the complex began to decompose. When the reaction temperature was above 260℃, th complex decomposed completely. No free DPPP was found in the experiment. The active complex (DPPP)Pd(OCOCF3)2 was formed when DPPP/Pd=1. The unactive complex (DPPP)2Pd(OCOCF3)2 was formed when DPPP/Pd>=2.

Key words REACTION MECHANISM COPOLYMERIZATION ETHYLENE CARBON MONOXIDE PHOSPHINE PALLADIUM PHOSPHORUS 31 MAGNETIC RESONANCE SPECTROMETRY

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