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催化、动力学与反应器

超临界溶液快速膨胀法制备二氯二茂钛微粒及催化乙烯聚合

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摘要 为克服茂金属催化剂得到的聚合物形态难以控制、表观密度较低、易粘釜和不适于气相淤浆聚合等缺点，以超临界溶液快速膨胀过程为手段，以期制得颗粒分布均匀的细微催化剂颗粒，继而得到形态良好的聚合物. 作为超临界流体技术的基础，首先测定了二氯二茂钛在超临界丙烷中的溶解度. 在此基础上，用RESS方法制得了均匀的超细催化剂颗粒，且系统考察了溶液浓度、预膨胀温度、喷嘴结构和接收距离对沉析颗粒粒径的影响. 最后，将RESS所制得的催化剂颗粒进行乙烯淤浆聚合，并分析聚合物形态结构. 实验结果表明，在温度为383.15～408.15 K和压力为10～35 MPa范围内，溶解度随温度的增加而增加，随压力的升高而增加，说明在该操作范围内，不存在反向区. RESS操作的结果显示，二氯二茂钛颗粒粒径随溶液浓度的增大而减小，随预膨胀温度的升高而增大，而喷嘴直径的减小和喷嘴长度的增加将使得颗粒粒径增大，而收集距离的增加将使得颗粒粒径先增加后减缓，直至不再变化. 通过对原始的催化剂颗粒和RESS制得的催化剂颗粒进行乙烯淤浆聚合表征发现，相比于原始催化剂，由于烯烃催化剂的复制原理，RESS制得的催化剂颗粒的聚合物具有良好的形态.

关键词 二氯二茂钛 超临界丙烷 溶解度 超临界溶液快速膨胀 乙烯聚合

分类号

FORMATION OF TITANOCENE DICHLORIDE MICROPARTICLES BY RAPID EXPANSION OF SUPERCRITICAL SOLUTION AND CATALYZED ETHYLENE POLYMERIZATION

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Abstract

One of the existing problems of metallocene catalyst is the difficulty in controlling its polymer morphology despite of its numerous advantages. According to the morphology replication nature of ethylene polymerization, polymer morphology could be improved by catalyst particle morphology improvement. The catalyst microparticles with narrow particle size distribution were obtained by rapid expansion from supercritical solution (RESS). Propane was chosen as a supercritical solvent and Cp_2TiCl_2 was selected as metallocene sample to catalyze ethylene in hexane medium. As a necessary fundamental research on rapid expansion of supercritical solution (RESS), the solubilties of titanocene dichloride in supercritical propane were measured by the static equilibrium method at temperatures from 383.15 to 408.15 K and pressure from 10.0 to 35.0 MPa. The solubility data were correlated with the Peng-Robinson (PR) equation of state and the AARD was 3.27%. RESS experiments were performed at different operation conditions, including solute concentration, pre-expansion temperature, nozzle length and diameter, and sample collection distance. The size of quasi-spherical and spherical particles formed in
the RESS process with several microns decreased with the increase of solution concentration, the decrease of pre-expansion temperature, the increase of nozzle diameter and the decrease of nozzle diameter. And the particle size increased with increasing collection distance until 87 mm. The catalyst particles were characterized through ethylene slurry polymerization to obtain the polymer. It was found that polymerization rate of ethylene was accelerated greatly and induced time was shortened for the RESS-reformed catalyst by comparing with the original catalyst particles. And the size distribution of reformed catalyst particles and the morphology of polymer were greatly improved.

Key words Cp_2TiCl_2 supercritical propane solubility RESS ethylene polymerization

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