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Effect of Graphene-Reinforced Ion-Exchange Resins on Catalytic Application

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Graphene has played an important role in nanoscience owning to its exceptional mechanical, electrical, chemical and thermal properties. Graphene-reinforced polymer nanocomposites (GPNCs) were prepared by *in situ* suspension polymerization, and the GPNCs were chloromethylated with chloromethyl ethyl ether and then aminated with trimethylamine to form GPNC ion-exchange resins (GPNC-IERs). Raman spectroscopy revealed the existence of chemically bonded interaction between graphene and the polymer networks *via* the increased intensity and Raman shifts. Theoretical simulation model developed using density functional theory indicated the mechanism of free radical polymerization, and the formation of strong sp^3 hybridization of C-C bond at graphene-polymer interface. The thermal and structural properties of the reinforced nanocomposites were investigated at the graphene contents varied from 0 to 1.0 wt%. The thermal stability was evaluated by thermogravimetric-differential thermal analysis (TG-DTA). It showed that the addition of graphene to the polymer matrix greatly increased the onset degradation temperature by about 20 °C. The prominent improvement of structural properties of the nanocomposites such as swelling capacity and total ion exchange capacity was found at 0.4 wt% graphene, which confirmed that the good dispersion of graphene throughout the polymer matrix with strong interaction within the networks counted for much in the properties enhancement effect. With the excellent swelling-resistance property and thermal stability, the GPNC-IER used as a catalyst exhibited a better catalytic performance in hydration of ethylene oxide (EO) to monoethylene glycol (MEG) in terms of activity and selectivity under lower water/EO molar ratio of 10. The 500h on-stream test further confirmed that graphene effectively reinforced the properties when well incorporated into the polymer networks.

Keywords: graphene; nanocomposite; ion exchange resin catalyst; ethylene glycol

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高性能石墨烯增强的离子交换树脂材料及其催化应用

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近年来，石墨烯等纳米碳材料以其优异的光电、导传热和力学性能在高聚物功能复合材料的制备方面引起广泛关注。将纳米碳材料与聚合物进行复合得到的聚合物纳米复合材料可以实现两者的优势互补。本工作在现有离子交换树脂材料催化剂的合成工艺基础上，结合纳米碳材料功能复合材料的增强机制，采用原位聚合法一步合成了石墨烯增强的复合型离子交换树脂材料。理论计算模型和表征结果表明，石墨烯可以有效分散于复合型树脂的聚合物基体中，并且石墨烯与聚合物碳链骨架之间存在着化学键合的强相互作用。经功能化后的复合型树脂材料的交换容量明显增大，树脂的热稳定性和抗溶胀性能均有大幅度提高，发生热分解起始温度提升近 20 °C。复合型离子交换树脂催化剂的耐溶胀、耐高温性能良好，成功地降低环氧乙烷催化水合的进料水比，提高了反应选择性。在环氧乙烷催化水合反应中，进料的水与环氧乙烷摩尔比为 10，石墨烯增强的复合离子交换树脂催化剂的催化活性、选择性和稳定性表现最好，平稳运行 500 小时保持乙二醇产品收率在 95%以上，反应后的树脂材料交换容量仍保持较高水平。

关键词：石墨烯；纳米复合材料；离子交换树脂催化剂；乙二醇