Controlled immobilization of methyltrioxorhenium(VII) based on SI-ATRP of 4-vinyl pyridine from halloysite nanotubes for epoxidation of soybean oil

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Abstract
Poly(4-vinylpyridine) (P-4VP) brushes of different lengths were grafted onto halloysite nanotubes (HNTs) by surface-initiated atom transfer radical polymerization (SI-ATRP) and methyltrioxorhenium(VII) (CH$_3$ReO$_3$, MTO) was immobilized onto HNTs through P-4VP brushes to catalyze epoxidation of soybean oil. 2-Bromoisobutyryl bromine was chosen as the initiator of SI-ATRP and anchored by reacting with hydroxyl groups of HNTs. To reduce the effect of 4-vinylpyridine on the initiator, Me$_6$tren as the ligand was introduced into the polymerization. The length of P-4VP brushes was controlled by the polymerization time. Through coordination between N in pyridine rings and MTO, a novel heterogeneous catalyst with different loadings of MTO for epoxidation of soybean oil was prepared. FTIR, TGA, TEM, GPC, UV–visible absorption spectroscopy and $^1$H NMR were used to characterize HNTs with P-4VP brushes and the heterogeneous catalysts. The results indicated that the length of P-4VP brushes increased with the polymerization time and MTO loading increased with P-4VP brush length. MTO molecules dispersed uniformly in P-4VP brushes and the heterogeneous MTO combined with H$_2$O$_2$ had good catalytic activity and selectivity to epoxidation of soybean oil. TOF of heterogeneous MTO increased with MTO loading and no ring-opening reaction occurred during epoxidation.

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1. Introduction

Epoxidation is one method of functionalizing plant oils and derivatives. Recently epoxidation of plant oil has been studied widely [1,2]. Various novel catalysts including ion-exchange resins, phosphotungstic acids, and enzymes have been tried to develop green, economical technological process of epoxidation. Methyltrioxorhenium(VII) (CH$_3$ReO$_3$, MTO) has obvious advantages to green, economical technological process of epoxidation. Methyltrioxorhenium(VII) (CH$_3$ReO$_3$, MTO) has obvious advantages to green, economical technological process of epoxidation. Methyltrioxorhenium(VII) (CH$_3$ReO$_3$, MTO) has obvious advantages to green, economical technological process of epoxidation.