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Dehalogenation of aromatic halides by polyaniline/zero-valent iron composite nanofiber: Kinetics and mechanisms

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ABSTRACT:

Dehalogenation of aryl halides was demonstrated using polyaniline/zero valent iron composite nanofiber (termed as PANI/Fe0) as a cheap, efficient and environmentally friendly heterogeneous catalyst. The catalyst was prepared via rapid mixing polymerization of aniline monomers with Fe(III) chloride as an oxidant followed by reductive deposition of nano-sized Fe0onto the PANI nanofiber using the by-products (Fe(II)/Fe(III)) present in the polymerization system as the Fe precursor. The catalyst was characterized by various physico-chemical techniques: ATR-FTIR, FE-SEM, HR-TEM, XRD, XPS and VSM. A mild reductive dehalogenation process of a wide range of aromatic bromides was explored in the presence of PANI/Fe0 catalyst. The catalyst was active and manifested a high reactivity (84% GC yield of naphthalene for 7 h at 40 °C) with four equivalents of t-BuMgCl. Deiodination reaction was proved to be more facile in comparison with their corresponding halides. Kinetic studies at different temperatures (30, 40, 50, and 60 °C) revealed an overall pseudo-first-order behaviour with rate constants 0.00281, 0.00893, 0.01137 and 0.02421 min-1, respectively. The reaction profile diagram of substrate consumption and the product formation rate indicated that there is no additional induction period was involved in the catalytic cycle. Activation energy (Ea) was calculated to be 56.3 kJ/mol through Arrhenius plot. Several deuteration experiments were conducted with different Grignard reagents to understand the mechanism of the reaction. These studies explained that the hydride incorporated product was obtained through ß-hydride elimination of t-BuMgCl. The catalyst was tested up to three cycles whereas the full conversion of the product was obtained for a prolonged period. PANI/Fe0 could be an alternative suitable catalyst for dehalogenation of environmentally poisonous aromatic halides.