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The heterogenization of L-phenylalanine–Ru(III) complex and its application as catalyst in esterification of ethyl alcohol with acetic acid

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A B S T R A C T

A simple route is demonstrated for the efficient immobilization of silica with L-(N- α -acetylphenylalanine)–ruthenium(III) complex. This catalyst was labelled as RHAPhe–Ru. The ²⁹Si MAS NMR showed the presence of T³, T², Q³ and Q⁴ silicon centers. The ¹³C MAS NMR showed the presence of three chemical shifts consistent with the three carbon atoms of the propyl group. The catalytic performance of RHAPhe–Ru was tested in the esterification of ethyl alcohol. A conversion of 82% was achieved, with 100% selectivity towards ethyl acetate. The catalyst could be regenerated by washing with ethanol and drying at 110 °C for 24 h without significant loss in reactivity.

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1. Introduction

The coordination and organometallic chemistry of amino acids with ruthenium is a research field of continuous interest (Sheldrick and Gleichmann, 1994; Urban et al., 1996; Rajkumar et al., 2009; Breivogel et al., 2011; Gujjarro et al., 2011). The literature showed that some Ru complexes can form an envelope conformation (Koch et al., 2002). The Ru complexes are used in such areas as to resolve and detect the enantiomers of racemic amino acids (Hockless et al., 1995; Dunina et al., 2000; Sheldrick and Exner, 1989), to prepare chiral catalysts for organic synthesis (Laurie et al., 1987; Katho et al., 2000), for the hydrogenation and transfer hydrogenation of imines by secondary alcohols (Kayak et al., 2008).

In recent years, the study of heterogenation of important organic ligands including important homogeneous catalysts onto suitable supports has seen increased activity due to the demand for environmentally friendly technologies and the propagation of green chemistry. We had recently shown that the immobilization of the silica surface with 3-(chloropropyl)triethoxysilane (CPTES) could be carried out via a simple and fast technique (Adam et al., 2009b). This

introduced the –CH₂–Cl functional end group on the silica surface. The –CH₂–Cl fragment was further used to heterogenize several organic molecules, i.e. saccharine (to form RHAC–Sac), melamine (to form RHAPrMela) and 7-amino-1-naphthalene sulfonic acid (ANSA) by a simple nucleophilic substitution reaction (Adam et al., 2009a, 2010, 2011). The saccharine, melamine and ANSA were shown to be an excellent homogeneous as well as a heterogeneous catalyst for the esterification of acetic acid with ethanol. Such type of modification is a significant contribution to green chemistry and the development of safer industrial techniques.

The esterification reactions are limited by slow reaction rates and is a reversible process. However, many catalysts were proposed for esterification. Mercs et al. (2007) have used fluoros ammonium salts to give 70–95% conversion of ester in toluene at 80 °C in 7 h. The use of N-(p-toluenesulfonyl)imidazole as catalyst for esterification was proposed by Rác et al. (2006) and gave a maximum of 95% conversion of ester in DMF in 7 h under reflux condition. Kovalchuk et al. (2009) used silica immobilized with [3-propyl-N-pyridinium, 3-propyl-N-methyl] or [3-propyl-N-butyl-imidazolium] salts as a heterogeneous catalyst for

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