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Catalysis and reaction mechanisms of *N*-formylation of amines using Fe(III)-exchanged sepiolite

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This study presents a rapid, economical and "green" *N*-formylation of anilines with formic acid (FA) using Fe(III)-exchanged sepiolite (IES) as a catalyst. The IES exhibited excellent catalytic properties and the reactions were complete within 20–90 min to afford products with high yields. The adsorption mechanism of FA on the IES sample was studied by infrared (IR) spectroscopy at a temperature range of 120–400 °C. The thermal desorption of pyridine was detected by the IR technique to estimate the acidity of IES. Lewis acid-bound pyridine bands at 1618–1631 cm^{-1} and 1443–1445 cm^{-1} were observed even after the IES sample was heated above 400 °C.

Keywords: sepiolite, ion-exchanged, *N*-formylation, formic acid, catalysis

Introduction

Due to its structural characteristics and physicochemical properties, sepiolite has recently been used as a catalyst support (Aramendía et al., 1994; Shimizu et al., 2004; Milt et al., 2010; Letaief et al., 2011; Karamanis et al., 2011). Also, the reactants are readily changed into activated complexes when the reactants are adsorbed due to basic [MgO_6] and acidic [SiO_4] centres on a sepiolite surface. The reactions catalysed by sepiolite are usually carried out under mild conditions with high yields and high selectivities and the procedure for these reactions is very simple.

N-Formylation of amines is an important reaction in synthetic organic chemistry. *N*-Formyl compounds are key intermediates in the synthesis of various pharmaceutical compounds (Chen et al., 2000). They are also useful reagents as Lewis base catalysts in allylation (Kobayashi & Nishio, 1994) and hydrosilylation of carbonyl compounds (Kobayashi et al., 1996). Various methods have been developed for the *N*-formylation of amines using different reagents such as ammonium formate (Reddy et al., 2000), formic acid and polyethylene glycol (PEG-400) (Das et al., 2008), formic acid and toluene (Jung et al., 2002), formic acid in the presence of TiO_2–SO_4^{2-} (Krishnakumar & Swaminathan, 2011), and formic acid using Zn metal as a catalyst under solvent-free conditions (Kim & Jang, 2010).

In the last decade, the modification of clays with Fe(III) species has been investigated in order to obtain Fe(III)-exchanged or Fe(III)-pillared materials. These materials have shown important potential applications as catalysts in organic synthesis (Dorado et al., 2006; Skoularikis et al., 1988; Long & Yang, 2000). To date, the synthesis of *N*-formyl compounds directly catalysed by raw or modified sepiolites has not been reported. Accordingly, an easy and efficient procedure for the synthesis of *N*-formyl compounds catalysed by Fe(III)-exchanged sepiolite (IES) is reported here. To explain the mechanism of reaction in the presence of the IES catalyst, infrared (IR) spectra of formic acid on IES were used to obtain information on the nature of the surface species and their mode of coordination. In addition, the acidic sites of IES were investigated using the IR spectroscopy technique with pyridine as a molecular probe.

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