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A new application for transition metal chalcogenides: WS_2 catalysed esterification of carboxylic acids

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Abstract

The first application of WS_2, a well-known graphene analogue, as a solid acid catalyst for carboxylic acid esterification is reported. WS_2 exhibits excellent specific activities and high conversion to methyl esters of (65-90 %) for C2-C16 carboxylic acid esterification with methanol under mild conditions, with Turnover Frequencies between 80-180 h^{-1}, and outstanding water tolerance even under equimolar water spiking. WS_2 also exhibits good stability towards methyl propanoate in the continuous esterification of propanoic acid, and is a promising candidate for biofuels production.

Keywords: Tungsten; Sulfide; Esterification, Carboxylic acid; Biofuels.

Introduction

Transition-metal chalcogenides (TMCs), particularly the group VI transition metal sulfides of W and Mo, have experienced a recent resurgence of academic interest because of their two-dimensional, ordered layered structures, and associated advantageous functional properties [1-3]. Akin to graphene, TMC sulphides are held together by strong intralayer covalent M-S bonds, with weaker Van der Waals interlayer interactions [4]. The resulting anisotropic layered structures offer excellent optical, electronic and mechanical properties, and hence a broad of applications as catalysts, lubricants, photoconductors, sensors, energy storage and medical devices (including drug delivery agents) [2, 4-6]. TMCs have been synthesised in a plethora of tunable morphologies, including nanotubes, nanoplates, nanorods, nanoflowers, nanowires and nanospheres, accompanied by diverse surface physicochemical properties [4, 7-9]. Although TMCs exhibit remarkable thermal and chemical stabilities due to their strong M-S bonding [10], the weak Van der Waals interlayer forces provide opportunities to prepare single and few layer nanosheets. Nanoparticulate and ultrathin TMC materials display unusual physical, chemical and electronic properties, particularly at their edges, compared to bulk analogues due to quantum confinement effects [3].