ISGC 2022

N°45 / OC
TOPIC(s) : Homogenous, heterogenous and biocatalysis / Clean reactions

Synthesis of Alkyl Substituted Phenols and Anilines through Hydrodeoxygenation using a Bimetallic Fe25Ru75@SILP Catalyst

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PURPOSE OF THE ABSTRACT

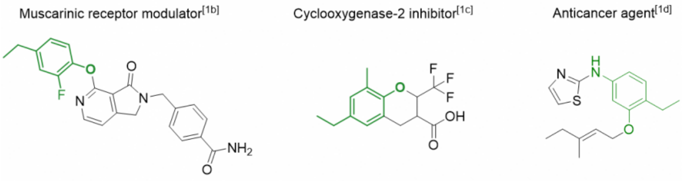
While alkyl phenols and anilines have attracted considerable attention due to their importance as building blocks for the production of fine chemicals, polymers, and pharmaceuticals (Figure 1),[1] their synthesis remains particularly challenging. In particular, conventional methods (i.e. direct alkylation, multistep approaches) present several limitations including poor selectivity, low tolerance toward functional groups, stoichiometric amount of toxic reagents and wastes, etc. Thus, the development of alternative methods providing easy access to these key motifs while being at the same time potentially more sustainable is important.

In this context, we propose to access alkyl phenols and anilines through the selective hydrodeoxygenation (HDO) of readily available hydroxy-, amino-, and nitro-acetophenone derivatives (Figure 2). For that, a catalyst capable of effectively hydrodeoxygenating ketones, while leaving the aromatic ring and other functionalities untouched is required. Recently, we have shown that a bifunctional catalyst composed of bimetallic Fe-Ru nanoparticles (NPs) immobilized on an acid-functionalized supported ionic liquid phase (Fe25Ru75@SILP+IL-SO3H) possess excellent activity and selectivity for the HDO of benzylic and non-benzylic ketones.[2] However, this catalyst could not be used for the HDO of hydroxy- or aminoacetophenone derivatives due to various acid-catalyzed side reactions.

In the present study, we tackle this challenge by utilizing an acid-free Fe25Ru75@SILP catalyst.[3] The mesomeric effects activating the ketone and stabilizing the intermediate carbocation were found to be the key to high HDO activity under acid-free conditions. Small (~3.3 nm) and well dispersed Fe25Ru75 NPs were synthesized in-situ in the SILP following an organometallic approach. The selective HDO of a large scope of hydroxy-, amino- and nitroacetophenone derivatives was achieved with excellent yields and selectivities, outlining the high tolerance of the catalyst toward various functional groups. The excellent catalyst stability and the possibility to switch back and forth between substrates were demonstrated under continuous flow conditions.

This opens a green and versatile route for the production of value-added phenols and anilines from widely available substrates. Future developments will involve the use of lignin-derived diketones as substrates.

FIGURES



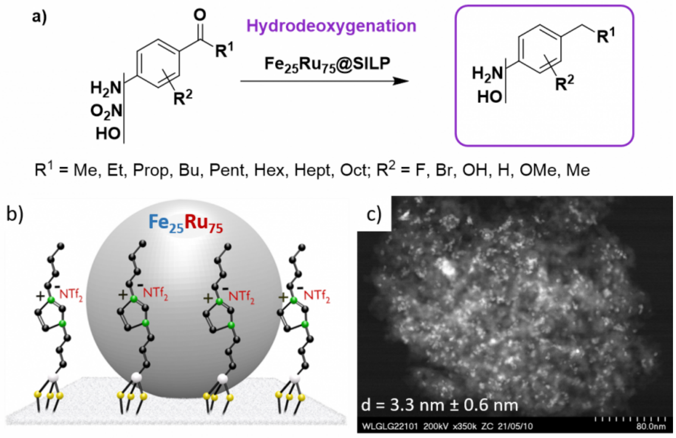


FIGURE 1

Examples for application of alkyl substituted phenols and amines.

FIGURE 2

Fe25Ru75@SILP catalyst

a) selective hydrodeoxygenation of amino, nitro and hydroxyacetophenone derivatives; b) schematic illustration of the catalyst; c) STEM-HAADF image of the Fe25Ru75@SILP catalyst.

KEYWORDS

selective hydrodeoxygenation | bimetallic | nanoparticles | SILP

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