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Selective Hydrogenation of CO2 to Formates Using Ruthenium Nanoparticles Immobilized on Supported Ionic Liquid Phases

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PURPOSE OF THE ABSTRACT

With the decline of fossil resources and the rise of alternative energy sources and chemical feedstock, the catalytic hydrogenation of carbon dioxide (CO2) using green molecular hydrogen is considered as a key transformation to integrate renewable energy and feedstock in the established chemical value chain.1 Among the various chemicals that can be produced from CO2 hydrogenation, formic acid/ formates are particularly interesting as they can act as liquid hydrogen carrier and feedstock chemical for further utilization.2 Over the past decades, several homogenous and heterogeneous catalysts have been developed to overcome the energy barrier to activate CO2 and selectively obtain formic acid/formates.3 In particular, combining metal nanoparticles (NPs) with functional solvents such as ionic liquids is attracting considerable attention to tune the molecular and electronic environment of NPs and improve activity and selectivity in CO2 hydrogenation to formic acid/formates. In this context, our group has shown that the immobilization of metal nanoparticles on molecularly modified surfaces (NPs@MMS), and in particular supported ionic liquid phases (SILPs), provides access to multifunctional catalytic systems that are versatile hydrogenation and hydrodeoxygenation catalysts.4

Capitalizing on this expertise, we report here the preparation of a series of Ru@SILP(R-X) catalysts (with R = cation functionality and X= anion), their characterization and application to the hydrogenation of CO2 to formate (Figure 1).5 The structure of chemisorbed ILs was systematically varied to study its influence on NP size and reactivity. Transmission electron microscopy measurements confirmed the presence of well-dispersed Ru NPs (0.8-2.9 nm) on all the SILPs.

Ru@SILP catalysts were found up to 10 times more active for the hydrogenation of CO2 in aqueous triethylamine than a reference Ru@SiO2 catalyst. In addition, clear changes in the Ru NPs reactivity were observed with variations in the molecular structure of SILP. Interestingly, the activity of sulfonic acid functionalized Ru@SILP materials was strikingly influenced by Ru loading, while no such impact was witnessed with neutral or amine functionalized catalysts. Mechanistic investigations confirmed that an intimate contact between the Ru and -SO3H as well as a carefully balanced Ru:-SO3H ratio are the key to observe sharply enhanced activities. The SO3H functionalities are presumably helping generate a denser hydrogen coverage at the surface of the Ru NPs, which in turn accelerates the rate-limiting step of formate desorption. After optimization of the reaction parameters, TONs as high as 16 111 were obtained, which is to the best of our knowledge the highest TON reported with supported nanoparticle catalysts. These results illustrate the potential benefits of designing and using NPs@SILP catalysts for CO2 hydrogenation, and can be further exploited to develop multifunctional systems containing SO3H-functionality that possess enhanced activity in formate production from CO2.

FIGURES

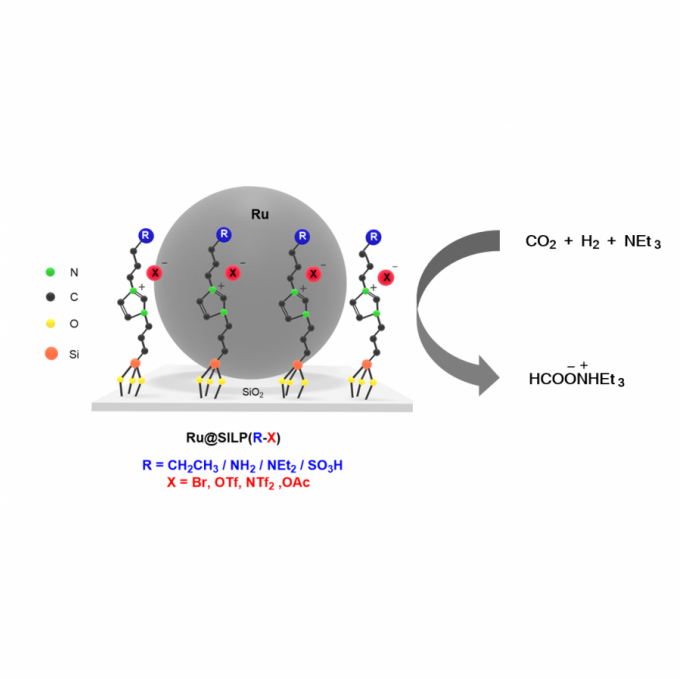

FIGURE 1

Our approach to the hydrogenation of CO2 using Ru@SILP(R-X) catalysts

Series of Ru@SILP(R-X) catalysts (with R = cation functionality and X= anion), and their application to the hydrogenation of CO2 to formate

FIGURE 2

KEYWORDS

Carbon dioxide | Formic acid/formates | Nanoparticle catalysts | Molecularly modified surfaces

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