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TOPIC(s) : Homogenous, heterogenous and biocatalysis

## Selective hydrogenation using bimetallic RhCo@SILP

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## PURPOSE OF THE ABSTRACT

The development of active and selective catalytic systems is a key step to a modern, sustainable chemical industry. In particular, hydrogenation catalysts displaying tunable selectivity are essential for the production of a wide range of products, such as renewable fuels, fine chemicals and pharmaceuticals.[1,2]

In this context, the synthesis of metal nanoparticles (NPs) in Supported Ionic Liquid Phases (SILP) produces NPs@SILP materials which are highly tunable (porous support, ionic liquid structure, metal NPs) and unite the advantages of NPs in Ionic Liquid (IL) catalysts with those of classical supported catalysts.[3] Typical key properties include a) enhanced NP stability due to the combination of electrosteric (IL-like layer) with steric (support material) stabilization, b) molecular tuning of the NPs reactivity by the IL-like layer, and c) direct implementation into continuous flow processes.[3] As a result, NPs@SILP catalysts have been proven to possess superior catalytic properties for a variety of transformations, especially for hydrogenation reactions.[3] One efficient strategy to tune the reactivity of NPs@SILP catalysts involves the synthesis of bimetallic NPs. For example, we have recently reported the synthesis of bimetallic FeRu NPs on SILPs (Fe<sub>25</sub>Ru<sub>75</sub>@SILP) for hydrogenation and hydrodeoxygenation reactions, where dilution of Ru with Fe led to a change in the selectivity of the catalyst.[4,5] In particular, addition of Fe enhanced activity for ketone reduction (compared to monometallic Ru@SILP) while simultaneously eliminating aromatic ring hydrogenation reactivity.

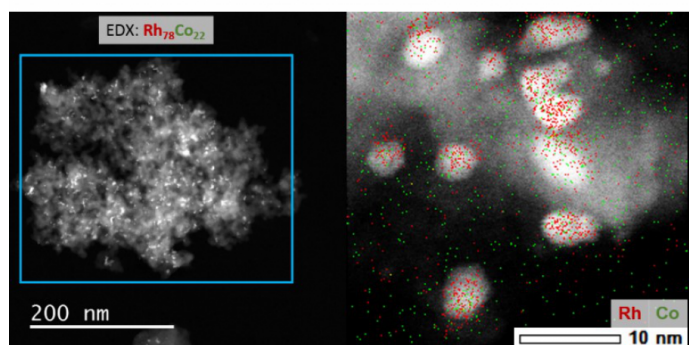
We report here a study on bimetallic NPs@SILP systems using combinations of Rh and Co. Following an organometallic approach, we have synthesized a wide range of Rh<sub>x</sub>Co<sub>1-x</sub>@SILP catalysts with finely controlled ratios of Rh/Co. Characterization of these materials with STEM-HAADF/EDX and SEM-EDS has evidenced the formation of small, well dispersed NPs containing both Rh and Co in their intended ratios (Figure 1). Preliminary XAS results of the Co K-edge indicate homogeneous alloying in the NPs.

Furthermore, we have investigated the activity of these Rh<sub>x</sub>Co<sub>1-x</sub>@SILP catalysts for the hydrogenation of benzylideneacetone (1) as a model substrate (Figure 2). While the completely saturated product 1d is produced in quantitative yields at high Rh contents (> 70 mol% Rh), a sharp change of selectivity is observed when the Rh content reaches 70 mol%. The catalyst is still able to efficiently hydrogenate the ketone, but leaves the aromatic ring untouched (product 1c). Interestingly, 1c can be produced in quantitative yield for Rh contents as low as 20 mol%.

Furthermore, Rh<sub>x</sub>Co<sub>1-x</sub>@SILP catalysts are highly active for the selective reduction of a broad scope of bicyclic heteroaromatics (e.g. benzofuran, indol, quinoline, benzothiophene) and derivatives thereof.

These results show that the immobilization of bimetallic RhCo nanoparticles on SILP support produces new materials possessing catalytic activities and selectivities which are not accessible using the pure metals.

## FIGURES

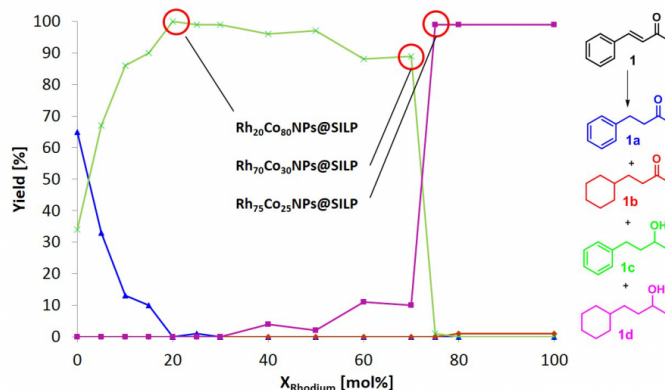


**FIGURE 1**

STEM-HAADF/EDX of Rh<sub>75</sub>Co<sub>25</sub>@SILP

red: Rhodium

green: Cobalt



**FIGURE 2**

Hydrogenation of 1 using Rh<sub>x</sub>Co<sub>1-x</sub>@SILP

Reaction conditions: Cat. (20,0 mg, 0.008 mmol [M]), H<sub>2</sub> (50 bar), substrate (0.80 mmol, 100 eq.), 150 °C, 16 h, mesitylene (0.5 mL). Yield determined by GC-FID using tetradecane as internal standard.

## KEYWORDS

bimetallic nanoparticles | SILP | selective hydrogenation

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