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Recent advances in soluble ruthenium(0) nanocatalysts and their reactivity

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ABSTRACT

Metal nanoparticles exhibit unusual properties different from metal complexes and heterogeneous metals and hence draw considerable attention for applications in catalysis, magnetism, medicine, optoelectronics, and sensors. Herein we present an overview of the recent progress in catalysis using soluble ruthenium nanocatalysts (colloids). These nanocatalysts have been widely used for catalyzing the hydrogenation of various substrates particularly arenes due to the milder conditions and the unique selectivities achieved compared to those exhibited by classical heterogeneous catalysts. Ru(0) colloids have been also examined for catalyzing many different reactions including transfer hydrogenation, dehydrogenation, coupling reactions and C—H activation, etc. Although in many of these transformations Ru(0) nanocatalysts exhibit high activities, there remain several challenges such as recovery of the soluble catalyst, catalysis by leached molecular clusters, and asymmetric catalysis with high enantioselectivity.

1. Introduction

Metal nanoparticles (MNPs) find exciting applications in chemistry, biology, microelectronics and nanoelectronics, due to their unusual optical, magnetic, and electronic properties [1–4]. In particular, MNPs of transition metals, have drawn wide attention as catalysts for various organic transformations in the industry and academia [5–11]. The interest in these nanoparticulate catalysts, also referred to as nanocatalysts is primarily driven by the assumption that carefully designed NPs can synergize the advantages offered by conventional homogeneous and heterogeneous catalysts. For example, the efficiency of nanocatalysts can be comparable to homogeneous catalysts as a large fraction of atoms is on the surface providing numerous active sites in comparison with heterogeneous catalysts [12]. At the same time, nanocatalysts provide the possibility for recovering and reusing the catalyst like heterogeneous catalysts. Consider magnetic NPs for example [12,13] or NPs dispersed in ionic liquids [14], they can be easily recovered from reaction mixtures and reused. MNPs possess unique activity and selectivity, which sometimes differ from the corresponding homogeneous metal complex catalysts [8,15].

The development of efficient and reproducible synthetic methods for small and monodisperse MNPs with a well-defined surface has facilitated their use in applications such as catalysis. Besides, advancements made with *in-situ* and *operando* characterization techniques to study the surface state of NPs have provided insights about the reaction sites and even reaction intermediates in some cases [14,16–29]. Continuous efforts are being devoted to the development of nanocatalysts with high efficiency, selectivity, recovery and reusability. Nanocatalysts particularly based on Pt, Pd, Rh and Ru have been extensively used for hydrogenation of olefins and arenes, polymerization, oxidation, and C—C coupling reactions [8,9,30–38].

Ruthenium is an excellent metal of choice in catalysis for both hydrogenation and oxidation reactions. Besides, the use of ruthenium is more economical due to its lower cost compared to other precious metals such as Pd and Rh. Organometallic complexes of Ru have demonstrated their effectiveness and selectivity in the homogeneous catalysis of organic transformations [39]. Designing nanocatalysts of Ru is a natural extension to molecular Ru catalysts. It is ideal to study ligand coordination to surface of Ru(0) nanoparticles (RuNPs) by NMR in solution or in the solid state, thanks to the absence of magnetic perturbations such as the Knight shift, paramagnetism, or ferromagnetism [40].

Various aspects of nanocatalysts have been reviewed [40,41,50,42–49]. In this review, we wish to primarily emphasize the catalysis carried out by unsupported soluble RuNPs (colloids) particularly examples reported after 2010. The nanocatalysts supported on solids that are promising to achieve catalyst recovery and reusability have not been covered in this review. Examples where MNPs act as mere supports are also beyond the scope of this review. A brief discussion about methods of preparation and various types of stabilizers precedes the discussion of their catalytic behavior.

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