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Review

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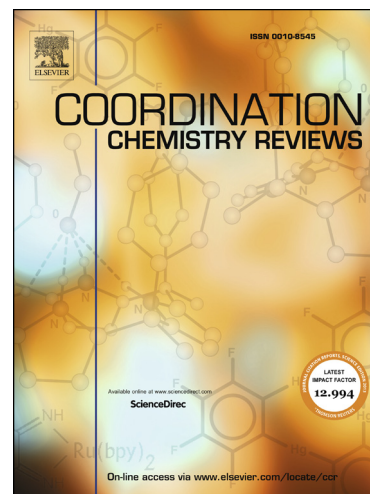
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Review

Surface Chemistry of Carboxylato-Substituted Metal Oxo Clusters – Model Systems for Nanoparticles

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Dedicated to Pierre Braunstein on the occasion of his 70th birthday

ABSTRACT

Clusters can be model systems for nanoparticles with regard to the chemistry of surface groups. Metal oxo clusters with carboxylato ligands are easily accessible and therefore well-suited for investigating the chemistry of cluster-bonded ligands. This review article gives an account on issues like ligand dynamics, post-synthesis ligand exchange, stability of the cluster core during ligand exchange, possible mechanisms of intra- and intermolecular ligand exchange or utilizing functional ligands.

Keywords: Ligand dynamics – Cluster rearrangement – Cluster degradation – Ligand exchange – Surface functionalization – Nanostructures

1. Introduction

A key issue in the chemistry of nanoparticles is their stabilization by means of suitable surface groups [1,2,3]. These groups not only prevent aggregation and growth of nanoparticles, but also control their shape and reactivity, interact with the environment, influence their physical properties and allow functionalization by organic groups. An understanding of the chemistry of the (mostly organic) groups attached to the nanoparticle surface is therefore of utmost importance.

Clusters can be model systems for nanoparticles with regard to the chemistry of surface groups, which can be the same as for nanoparticles of the same composition. They are called “ligands” in the remainder of this article, because their bonding characteristics and the other issues discussed here are equivalent to what is known from coordination chemistry. Investigating clusters has several advantages compared with nanoparticles. Clusters have clearly defined structures (no size distribution) and can be investigated with molecular chemistry methods. Furthermore, bonding of ligands in chemically non-equivalent positions at the cluster surface can be distinguished.

This article concentrates on titanium and zirconium oxo clusters, preferentially with carboxylato and alkoxo surface groups. They have typical diameters in the range 0.8–1.5 nm. Clusters of this type have been investigated in more detail than others, because they are easily prepared by reaction of the corresponding metal alkoxides and carboxylic acids, and many

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