PHOSPHORUS, SULFUR, AND SILICON
2017, VOL. 192, NO. 8, 977–983
https://doi.org/10.1080/10426507.2017.1322083

Taylor & Francis
Taylor & Francis Group

Synthesis and spectroscopic characterization of tris(*tert*-butoxy)siloxy titanium and hafnium complexes: Molecular precursor to [M/Si/O (M = Ti, Hf)] materials

Mohan Gopalakrishnan[a,b], Swaminathan Shanmugan[c], and Nallasamy Palanisami[a]

[a]Department of Chemistry, School of Advanced Sciences, VIT University, Vellore, Tamil Nadu, India; [b]Department of Chemistry, Karpagam University, Coimbatore, Tamil Nadu, India; [c]Research Institute & Department of Chemistry, SRM University, Kattankulathur, Tamil Nadu, India

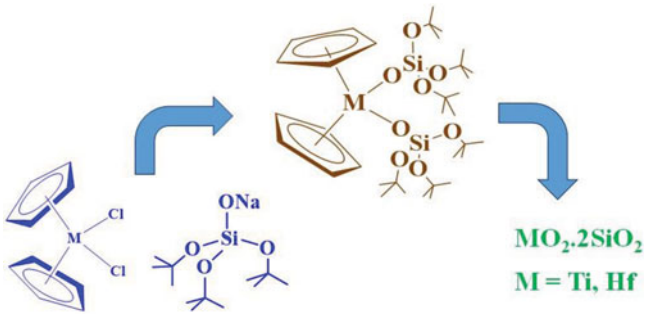
ABSTRACT

The reaction of one equivalent of metallocene dichloride Cp_2MCl_2 (M = Ti, Hf) with two molar equivalents of sodium salt of tri(*tert*-butoxy)siloxane, $(^tBuO)_3SiONa$, in toluene yields $Cp_2Ti[OSi(O^tBu)_3]_2$ (**1**) and $Cp_2Hf[OSi(O^tBu)_3]_2$ (**2**). These compounds were characterized by analytical and spectroscopic techniques (C/H/N analysis, FT-IR, NMR, EI-MS, and thermal analysis). An independent thermolysis of **1** and **2** at low temperature resulted in the formation of the corresponding metal silicates $MO_2{\cdot}2\ SiO_2$ [M = Ti (**3**) and Hf (**4**)] as evidenced by infrared spectroscopy, powder X-ray diffraction analysis (PXRD), and scanning electron microscopy (SEM). These thermally stable amorphous metal silicate materials (**3** and **4**), albeit exhibiting moderate surface areas, are found to be microporous by N_2 adsorption studies. UV-vis-NIR spectroscopy shows low energy band gap E_g = 2.63 eV for **3** and 2.99 eV for **4** due to the silicon oxide mixed with the corresponding transition metal oxides. The photocatalytic activity of titanium silicate material (**3**) has been explored in terms of degradation of methylene blue.

ARTICLE HISTORY
Received 1 July 2016
Accepted 19 April 2017

KEYWORDS
Metallasiloxanes; photocatalyst; surface area; thermolytic degradation

GRAPHICAL ABSTRACT



Introduction

The development of advanced materials with tailored properties frequently requires low-temperature methods to permit the formation of metastable structures.[1–3] Sol-gel method has attracted great interest as a low-temperature route for the synthesis of metal oxide materials *via* the hydrolysis/condensation of alkoxide precursors.[4,5] However, there are still difficulties in controlling the atomic structures of sol-gel derived products, because the rates of hydrolysis for different metal precursors in a polar solvent vary drastically.[6,7] An alternative approach for the synthesis of homogenous metal oxide materials implies the use of single-source molecular precursors that exhibit advantages including well-defined stoichiometries, efficient incorporation of building blocks, kinetically controlled reaction pathway and low temperature routes to metastable structures. In this context, Tilley et al. studied the use of single source precursors of metal siloxanes for the synthesis of corresponding silicate materials at elevated temperature. For example, transition-metal and main-group metal complexes containing the oxygen-rich ligand $-OSi(O^tBu)_3$ have been used as single-source precursors to produce homogeneous metal silicate materials (M/Si/O) due their clean thermal decomposition at low temperatures (~300°C) *via* the elimination of isobutene and water.[8–12] Thermolytic molecular precursor approach is a promising method to generate metal silicate materials by homogeneous incorporation of the metal into the structure, particularly at high metal loadings. Such high dispersions are difficult to achieve by wet impregnation methods, because metal oxide domains tend to form under aqueous conditions. Over the past decade few research group have been investigating the synthesis of metal silicate

CONTACT Nallasamy Palanisami palanisami.n@gmail.com Department of Chemistry, School of Advanced Sciences, VIT University, Vellore 632 014, Tamil Nadu, India.
Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gpss.
Supplemental data for this article can be accessed on the publisher's website at https://doi.org/10.1080/10426507.2017.1322083