Journal of Colloid and Interface Science 459 (2015) 17–28

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis

Structural and thermal properties of inorganic–organic montmorillonite: Implications for their potential environmental applications

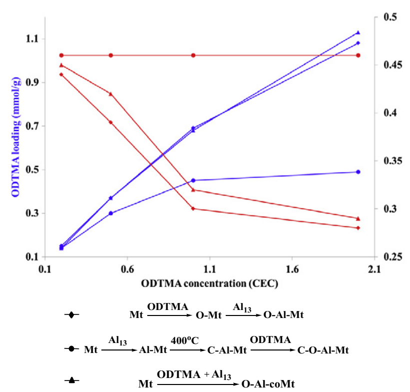
Suramya I. Rathnayake, Yunfei Xi, Ray L. Frost, Godwin A. Ayoko *

Discipline of Nanotechnology and Molecular Science, School of Chemistry, Physics and Mechanical Engineering, Queensland University of Technology (QUT), GPO Box 2434, Brisbane, Queensland 4001, Australia

HIGHLIGHTS

- Inorganic–organic montmorillonite were prepared using three intercalation methods.
- Laser ablation technique was used for elemental analysis.
- Surfactant loading depends on the intercalation method and surfactant concentration.
- Aluminium-pillars are fixed within the interlayers by calcination.
- Calcined interlayers cannot change by subsequent surfactant introduction.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 3 June 2015
Revised 25 July 2015
Accepted 30 July 2015
Available online 31 July 2015

Keywords:
Montmorillonite
Octadecyltrimethylammonium bromide
Organoclay
Hydroxy aluminium polycation
Aluminium-pillared clay
Inorganic–organic clay

ABSTRACT

Inorganic–organic clays (IOCs), clays intercalated with both organic cations such as cationic surfactants and inorganic cations such as metal hydroxy polycations have the properties of both organic and pillared clays, and thereby the ability to remove both inorganic and organic contaminants from water simultaneously. In this study, IOCs were synthesised using three different methods with different surfactant concentrations. Octadecyltrimethylammonium bromide (ODTMA) and hydroxy aluminium ($[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ or Al_{13}) are used as the organic and inorganic modifiers (intercalation agents). According to the results, the interlayer distance, the surfactant loading amount and the Al/Si ratio of IOCs strictly depend on the intercalation method and the intercalation agent ratio. Interlayers of IOCs synthesised by intercalating ODTMA before Al_{13} and IOCs synthesised by simultaneous intercalation of ODTMA and Al_{13} were increased with increasing the ODTMA concentration used in the synthesis procedure and comparatively high loading amounts could be observed in them. In contrast, Al/Si decreased with increasing ODTMA concentration in these two types of IOCs. The results suggest that Al-pillars can be fixed within the interlayers by calcination and any increment in the amount of ODTMA used in the synthesis procedure did not affect the interlayer distance of the IOCs. Overall the study provides valuable insights into the structure and properties of the IOCs and their potential environmental applications.

1. Introduction

Many industrial and municipal wastewaters generally contain both inorganic and organic pollutants, which essentially require

* Corresponding author.
E-mail address: g.ayoko@qut.edu.au (G.A. Ayoko).

http://dx.doi.org/10.1016/j.jcis.2015.07.071

treatment before they are released into the environment due to their harmful impacts on human health and ecosystems [1,2]. Hence there is an urgent need to find an efficient and inexpensive method to remove inorganic and organic contaminants simultaneously from polluted water.

Naturally abundant clay minerals are inexpensive precursor that can be used as low cost adsorbents due to their unique properties. Smectite clays (e.g. montmorillonite) show high cation exchange capacity (CEC) (80–120 meq/g), high surface area, micro and meso-porosity and swelling properties [3,4]. Montmorillonite exhibits one octahedral layer made with octahedral $[AlO_3(OH)_3]^{6-}$ sandwich between two tetrahedral layers made with tetrahedra $[SiO^4]^{4-}$. Several octahedra and tetrahedra are connected by sharing three oxygen atoms to form octahedral and tetrahedral sheets, respectively. The clay layers are negatively charged due to the isomorphous substitution of Si^{4+} and Al^{3+} by cations with lower charges, and the negative charge is counterbalanced by absorbing exchangeable cations, usually alkaline or alkaline earth metals on the edges and in between the layers [5,6]. Negatively charged hydrophilic clay layers and broken edges attract species with opposite charges such as organic cations and heavy metal ions [7]. But clay minerals are ineffective for the adsorption of non-ionic and non-polar organic compounds (NOCs) in aqueous solutions [8–10]. The nature of the clays can be modified by replacing the exchangeable cations with organic cations, most commonly quaternary alkyl ammonium cations which make clay surfaces hydrophobic and increase the adsorption capacity towards non-ionic and NOCs. Smectites, being strongly hydrophilic, have significant adsorption capacities towards harmful ionic inorganic water contaminants [11–13] which can be increased by intercalating smectites with pillaring agents such as metal oxide cations to produce pillared clays. The most commonly used inorganic pillaring agent is hydroxy aluminium polycation (Al_{13}) and Al-pillared clays (Al-Mt) are obtained by the intercalation of Al_{13} cations which exchange the interlayer cations of clay followed by dehydration and dehydroxylation upon calcination to give Al_2O_3 like-clusters [14]. They act as pillars separating adjacent silicate layers and increasing the basal spacing and creating permanent porosity [15]. Al-pillared clays are more thermally stable and more porous than organoclays, and can be used to remove heavy metals [12,16] and oxyanionic contaminants such as chromate (Cr(VI)) and phosphate [17,18] from water.

Studies have been conducted in modifying clays with both inorganic modifiers such as metal hydroxy polycations and organic modifiers such as cationic surfactants in order to obtain hydrophobic/organophilic clays with high thermal stability and porosity as early as 1990 and the resultant clays are named as inorganic–organic clays (IOCs) [19]. According to the literature, they have the ability to remove both inorganic and organic contaminants simultaneously from water. Simultaneous adsorption of dodecane (hydrocarbon) and metal cations (Pb^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+}) [20], para-nitrochlorobenzene and Cr(VI) [21], phenol and phosphate [22], naphthalene and phosphate [23] have been investigated and the IOCs show high adsorption capacity towards a wide range of organic and inorganic contaminants. The most commonly used organic modifier and inorganic modifier in the preparation of IOCs is hexadecyltrimethylammonium bromide (HDTMA) and Al_{13} [22,24–27].

IOCs have a wide variety of applications as adsorbents in wastewater treatment because the structure (e.g. interlayer distance, pore size) and properties (hydrophobicity, surface charge) can be adjusted to suit the application by varying the organic modifier (usually alkyl ammonium cations with different chain lengths and different number of substituents) and/or inorganic modifier (different metal hydroxy polycations changing the pillar size and the distance between the pillars). For example, hydroxy polycations of Fe(III), Cr(II) and Ti(II) can be used as inorganic modifier and the pillaring agent in IOCs instead of hydroxy aluminium, and the resultant IOCs are effective adsorbents towards nitrophenol, basic yellow 28 dye [28], Supranol yellow 4 GL [29], herbicide diuron [30] and dye sulfacid brilliant pink [31]. Also, mixed metal (Fe/Al) pillared IOCs with improved structure and properties shows promising adsorption capacity towards both inorganic water contaminants (e.g. Cu^{2+}) and organic water pollutants (e.g. phenol) [32]. Phenol and its chloro and nitro derivatives are most common water pollutants present in all types of wastewaters and IOCs shows high affinity towards these water pollutants [24,31,33,34].

According to the literature, the structure and properties of IOCs strongly depend on the intercalation method (the sequence of introducing inorganic and organic modifier) and the ratio of inorganic and organic modifiers (concentration of surfactant and the metal hydroxy polycation used in the synthesis procedure) [21,23]. Three different methods of synthesising IOCs have been reported; (i) cationic surfactant intercalation into montmorillonite before metal hydroxy polycation intercalation (ii) cationic surfactant intercalation into montmorillonite after metal hydroxy polycation intercalation and (iii) simultaneous cationic surfactant and metal hydroxy polycation intercalation into montmorillonite [21,23,35,36]. Recently, the influences of the calcination temperature of the pillared clays and the used dosage of surfactant on the interlayer structure and the thermal stability of IOCs synthesised by intercalating Al_{13} first and then HDTMA were investigated [27].

To best of our knowledge, ODTMA has not been used in IOCs synthesis and no comprehensive studies have been conducted to determine the effect of surfactant concentration (the ratio of surfactant/metal hydroxy polycation) used in the synthesis procedure on the structure and the properties of the IOCs synthesised by the three methods mentioned above. Although ODTMA modified organoclays have been reported [37–39] more studies are required for the clear understanding of the structure and properties of IOCs synthesised using ODTMA as the organic modifier and Al_{13} as the inorganic modifier. Therefore, the aim of the study is to determine the effect of surfactant concentration used in the synthesis process (the organic and inorganic modifier ratio) on the structure and the properties of IOCs and to explore the probable applications of the resultant IOCs for the removal of both recalcitrant inorganic and organic pollutants from wastewater. In order to fulfil these aims, a series of IOCs were synthesised using Al_{13} and ODTMA as inorganic and organic modifiers, respectively. ODTMA concentration used in the synthesis procedure was varied and three different methods were employed in the synthesis of IOCs. The structure and properties of the resultant IOCs were investigated and compared with that of organoclays with different ODTMA loadings and Al-pillared clays. Changes in the interlayer distance of these modified clays due to intercalation of ODTMA and Al_{13} were determined by the X-ray diffraction (XRD) technique. The thermal stability of IOCs synthesised using different intercalation methods at different ratios of ODTMA/Al_{13} was evaluated by thermogravimetric analysis (TG) and derivative thermogravimetric analysis (DTG). Furthermore, the TG/DTG results can be used to determine the different environments of the surfactant and thermal stability within the clay layers. Laser ablation inductively coupled plasma mass spectroscopy (LA-ICP-MS) was employed to determine the intercalated Al_{13} into IOCs. Although, X-ray fluorescence spectroscopy (XRF) is the most commonly used method for this purpose [16,27,32], in this study the applicability of LA-ICP-MS to determine Al/Si ratio of Al pillared clays and IOCs was explored.