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Review article

Synthesis of iron-rich tri-octahedral clay minerals: A review

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ABSTRACT

Examples in materials science and in geology show an interest for iron-rich tri-octahedral clay mineral synthesis in large amounts and with well-defined characteristics. This review summarizes previously reported methods and conditions for iron-rich tri-octahedral clay mineral synthesis. Two approaches of hydrothermal synthesis have been applied: using gel or solid precursors. The most common synthesis approach is the hydrothermal synthesis using gel precursor. The synthesis of 1:1 type clay minerals were performed in reducing conditions in neutral or alkaline pH at various temperature and time ranges. The experimental conditions for 2:1 type clay mineral synthesis were in most cases similar to 1:1 type clay minerals, with in addition acidic pH and oxidizing conditions. The most commonly used methods for identifying and characterizing these minerals are X-ray diffraction, infra-red and Mössbauer spectroscopies as well as transmission electron microscopy. The thermodynamic stability of synthesized phases, as well as the reason for elements adopting a definite configuration and distribution in solid phase remain open questions.

1. Introduction

Iron-rich tri-octahedral clay minerals have a high potential as heterogeneous catalyst, e.g. in Fenton-like reactions (Garrido-Ramírez et al., 2010; Li et al., 2015; Wang et al., 2017) and some organic transformations (Arundhathi et al., 2011; Arundhathi et al., 2010; Sreedhar et al., 2009). In nature, these minerals are found in ocean floors, where the serpentinization of olivines occurs (Kodolányi et al., 2012), but such formations are either not easily accessible or not largely abundant. Moreover, natural minerals often contain other mineral phases, which can be considered as impurities for certain applications. To obtain a sufficient amount of pure iron-rich tri-octahedral clay minerals and to study their potential application in catalysis, their synthesis can be foreseen.

Apart for the interest of the application in materials science, clay minerals are also present in deep-geological formations envisaged for CO_2 sequestration or nuclear waste disposal (Bourg, 2015; Grambow, 2016). To predict a long-term stability of these formations, geochemical modelling is often performed, but the lack of thermodynamic data regarding iron-rich tri-octahedral clay minerals places limits to these models. An investigation of the thermodynamic properties of synthetic iron-rich tri-octahedral clay minerals as analogues to naturally formed minerals could provide the missing data. Thus, this could improve our understanding of the long-term stability of these minerals and the respective geological formations in which their natural analogues are present.

The third aspect, where the importance of the presence of iron-rich swelling clay minerals has been suggested is the formation of the first biopolymers on Earth surface (Feuillie et al., 2013; Meunier et al., 2010; Pedreira-Segade et al., 2016). A series of synthetic iron-rich tri-octahedral clay minerals with well-defined characteristics, such as particle size and layer charge could contribute to understanding the adsorption and retention phenomena of these molecules on clay surfaces.

Finally, the presence of iron-rich tri-octahedral clay minerals has been observed on the surface of Mars (Chemtob et al., 2015), in deep-sea sediments (Baldermann et al., 2015; Tosca et al., 2016), during the chloritization (Beaufort et al., 2015) and serpentinization (Kodolányi et al., 2012) in subduction zones and transform faulting, in meteorites (Zolotov, 2015), but the formation conditions remain poorly understood. Their synthesis under well-controlled conditions and parameters could help to understand these phenomena.Previously mentioned examples in materials science and in geology show an interest for iron-rich tri-octahedral clay mineral synthesis in sufficient quantities and with well-defined characteristics. The first report of iron-rich tri-octahedral clay mineral synthesis dates back to 1911 (Van Hise and Leith, 1911), but there has been a growing interest particularly in the latest years (Baldermann et al., 2014; Chemtob et al., 2015; Tosca et al., 2016). Although three general reviews on clay mineral synthesis by Kloprogge et al. (1999), Zhang et al. (2010) and Jaber et al. (2013) exist, as well as a review of Petit et al. (2017) on Fe-rich smectites has

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been recently published, ferrous iron-rich systems are very particular in terms of synthesis conditions (atmosphere, redox potential) and characterization, making it necessary for a separate review. Three different clay mineral synthesis techniques are known: synthesis from dilute solution, solid-state and hydrothermal synthesis (Carrado et al., 2006). Different variations of hydrothermal synthesis technique have been used to form iron-rich tri-octahedral clay minerals (IRTOCM). They can be divided into two groups based on the type of precursor used: (1) hydrothermal synthesis using gel precursor and (2) hydrothermal synthesis using solid precursor. These two groups are discussed in this review focusing on the initial reactants, conditions, and procedures. This information is then summarized with respect to each mineral type: saponite (2:1 type), serpentine (1:1 type) and chlorite groups. The spectroscopic methods used to characterize iron-rich clay minerals have been previously summarized (Neumann et al., 2011), therefore only brief description of techniques used for IRTOCM identification is mentioned. At the end, the use of IRTOCM in geochemical simulations and the influence of element speciation in solution on the neoformed phases are discussed.

2. Hydrothermal synthesis based on the use of gel precursor

2.1. Procedure of synthesis

The hydrothermal synthesis method based on the use of gel precursor is the most common to form IRTOCM. A general procedure composed of five steps can be suggested (Fig. 1):

1) preparation of a precursor;
2) gel processing;
3) hydrothermal treatment;
4) product processing;
5) storage.

2.1.1. Preparation of a precursor

The synthesis procedure starts with the preparation of a precursor, where an exact known mass of solid compounds or a defined volume of solutions is taken in stoichiometric proportions corresponding to the desired chemical composition of the product. In both cases, whether solid compounds or solutions are used, there are two ways of combining the constituents. In the first case, the order of mixing is the following: (1) metal Fe, Mg or Al salt solutions, (2) source of Si and (3) mineralizing agent (e.g., OH^-). In the second case, the salt solution containing Fe, Mg and/or Al (A) and a solution containing Si and OH^- (B) are mixed separately. Then solution (B) is slowly added to solution (A). After the addition of all the compounds, precipitation of solid phase occurs, often as a gel. A gel is a non-fluid colloidal network containing lamellar or disordered structures that are expanded throughout whole volume of gel by a fluid (McNaught and Wilkinson, 1997). Less often, precipitated solid phase remains dispersed in the solution in form of suspension. Ideally, the preparation of precursor should result in a homogenous distribution of various elements in the gel matrix (Hamilton and Henderson, 1968), but in practice the formation of clusters of elements can occur. This can generate a heterogeneous distribution of certain elements in the precursor and subsequently the final product can also exhibit some sort of heterogeneity. After the preparation of precursor, depending of the metal source, washing or heating of precipitate can be performed.

2.1.2. Different types of subsequent precursor treatment

Three different approaches can be distinguished for the following synthesis procedure. The first type of approach consists of a gel aging step only. After precipitation of the solid phase, the dispersion is left to age for several weeks or months (Decarreau, 1981; Farmer et al., 1991; Harder, 1978; Tosca et al., 2016). The gel aging step is performed at temperatures ranging from 3 °C to 120 °C. For the second approach, gel aging is followed by hydrothermal treatment (Chemtob et al., 2015; Grauby et al., 1994; Lantenois et al., 2005; Mizutani et al., 1991; Wilkins and Ito, 1967). The hydrothermal treatment step is performed in autoclaves at temperatures from 60 °C to 600 °C over the course of 1 day to 3 months. In the third approach, only hydrothermal treatment is applied (Baldermann et al., 2014; Boukili et al., 2015; Flaschen and Osborn, 1957; Grubb, 1971; Roy and Roy, 1954). Another approach, which was used to obtain the first synthetic clay minerals in laboratory but is no longer in use, consisted of precipitating the solid from dilute solutions at boiling temperature under reflux (Caillère et al., 1953).

A one-step synthesis consisting solely of a gel aging or hydrothermal step have been applied in the studies which focus on the formation conditions of IRTOCM in specific geological environments (Baldermann et al., 2014; Boukili et al., 2015; Chemtob et al., 2015; Decarreau, 1981; Farmer et al., 1991; Flaschen and Osborn, 1957; Grubb, 1971; Harder, 1978; Roy and Roy, 1954; Tosca et al., 2016; Van Hise and Leith, 1911). A two-step synthesis including both gel-aging and hydrothermal steps has been applied in some cases, where a known and precise material chemical composition is needed (Grauby et al., 1994; Lantenois et al., 2005; Mizutani et al., 1991; Wilkins and Ito, 1967). The heating or washing of sample between the two steps allows removing salts such as nitrates and carbonates so that the precursor's chemical composition corresponds to the one expected for the final product. In practice, the complete washing of anions is impossible in a gel, therefore some deviation from 'ideal composition' should be expected. A one-step procedure consisting solely of hydrothermal treatment could be applied in studies where simple and fast procedure is needed and the presence of impurities can be tolerated.

2.1.3. Product processing and storage

The processing block includes washing and/or heating of the products. The washing procedure in order to remove the impurities within the neoformed products varies from one synthesis procedure to another, including steps such as centrifugation, filtration and dialysis. The

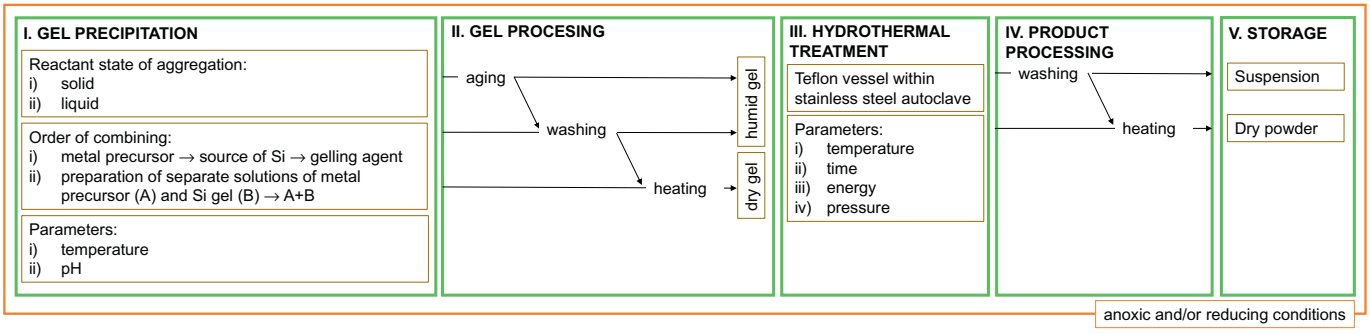

Fig. 1. 5-block action scheme detailing the steps of hydrothermal synthesis procedure based on the use of gel precursor for iron-rich trioctahedral clay minerals: (I) gel precipitation, (II) gel processing, (III) hydrothermal treatment, (IV) product processing and (V) sample storage.