Applied Clay Science 161 (2018) 103–109

Contents lists available at ScienceDirect

Applied Clay Science

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

Research paper

Improvement in phase purity and yield of hydrothermally synthesized smectite using Taguchi method

Bing-Sheng Yu*, Yi-Yu Liu

Institute of Mineral Resources Engineering, National Taipei University of Technology, No.1, Sec. 3, Chung-Hsiao East Road, Taipei 10608, Taiwan

ARTICLE INFO

Keywords:
Hydrothermal synthesis
Smectite
Taguchi method
Rietveld method
Phase purity
Yield

ABSTRACT

Smectite is widely used in many industrial fields and material applications. Although the high phase purity and yield of synthetic smectite are paramount for advanced applications, few studies have investigated these aspects. In this work, the phase purity and yield of synthetic smectite were estimated for the first time using a quantitative phase analysis through X-ray diffraction and Rietveld method software. The Taguchi method was used to optimize the phase purity and yield of synthetic smectite, and the effects of synthesis factors are discussed. Based on the trioctahedral smectite formula $Na_{2x}(Al_{2(1\text{-}x)}Mg_{2x}\square)Si_4O_{10}(OH)_2$, an $Na_2O\text{-}MgO\text{-}Al_2O_3\text{-}SiO_2\text{-}H_2O$ system was used for smectite synthesis at temperatures of 200 °C and 220 °C, for durations of 48–96 h and pH values of 7, 9, and 11. The results indicate that the duration, starting material, and type of mineralizer are the three most important factors affecting the phase purity and yield of synthetic smectite. For the synthesis conditions optimized by the Taguchi method in this study, the phase purity and yield of the synthetic smectite can reach up to 92.5% and 88.3%, respectively. These results can contribute to an improved understanding of the factors that control the phase purity and yield of synthetic smectite and provide an efficient method for the synthesis of high-quality smectite for advanced applications.

1. Introduction

Smectite has a 2:1 layer structure that consists of an octahedral sheet intercalated between two tetrahedral sheets. Smectite has a favorable expansion ability and cation exchange capacity because of its unique crystal structure. It yields X-ray diffraction (XRD) patterns characterized by basal reflections that vary with humidity, exposure to certain organic molecules, heat treatment, and exchangeable cations (Wilson, 1987). When saturated with ethylene glycol, the 001 reflection of most smectites swells to approximately 17 Å (approximately 17.8 Å with glycerol); when heated to 400 °C, the 001 reflection collapses to approximately 10 Å (the exact extent of collapse is often related to the exchange cations present and to the smectite itself). The cation exchange capacity of relative pure smectite ranges from 70 to 130 cmol (+)/kg (Odom, 1984).

Because of its high cation exchange capacity and large specific surface area, smectite has been widely applied in various areas, including biomedicine (e.g., drug carriers) (Feng et al., 2009), materials science (e.g., fining agent, raw material of drilling fluids, metal casting, ceramic and fillings, and support of semiconductor nanoparticles) (Qin et al., 2005; Eisenhour and Brown, 2009; Ghadge and Ghangrekar, 2015; Intachai et al., 2017), and environmental remediation (e.g., adsorbents and catalyst supports, adsorbent of hazardous substance, and barrier to high-level radioactive waste) (Barama et al., 2009; Gates et al., 2009; Eisenhour and Brown, 2009; Natkański et al., 2013; Zhu et al., 2016).

The ideal formula of smectite is $Na_{2x}(Al_{2(1-x)}Mg_{2x})(Al_ySi_{4-y})O_{10}(OH)_2$, where **x** represents the theoretical octahedral sheet substitution rate (i.e., the rate of Al–Mg substitution) and **y** represents the theoretical tetrahedral sheet substitution rate (i.e., the rate of Al–Si substitution). Various deposits have different structural compositions, phases, and impurities, all of which may limit the potential use of smectite without pretreatment. These problems can be overcome by varying mineral synthesis conditions (Reinholdt et al., 2005). Several researchers have attempted to synthesize smectites by using different conditions, such as a low temperature and pressure (< 100 °C and 1 bar, respectively), hydrothermal conditions of 100 °C–1000 °C at P_{water} or high pressure, and a temperature of > 1000 °C at a very high pressure (Kloprogge et al., 1999).

Studies have suggested that the interlayer species can influence the characteristics of montmorillonite (e.g., thermal stability) (Chen et al., 2017; Zhang et al., 2017). To obtain high-quality smectite for advanced applications, numerous researchers have attempted to synthesize smectite containing different ions, such as Mn, Fe, Co, Ni, Cu, and Zn, in

* Corresponding author.
E-mail address: bing@ntut.edu.tw (B.-S. Yu).

https://doi.org/10.1016/j.clay.2018.04.001
Received 6 October 2017; Received in revised form 27 March 2018; Accepted 2 April 2018
0169-1317/

the interlayer (Prihod'ko et al., 2004; Higashi et al., 2007; Trujillano et al., 2009, 2015). For advanced applications of synthetic smectite, high phase purity and yield are extremely crucial. However, the synthesis of high-purity smectite remains difficult (Kloprogge et al., 1999). To the best of the authors' knowledge, few studies have quantitatively discussed phase purity and yield for smectite synthesis.

In this study, trioctahedral smectite was synthesized using the hydrothermal method, and, for the first time, the phase purity and yield of synthetic smectite were estimated using quantitative phase analysis through XRD and BGMN Rietveld method software (Bergmann et al., 1998).

Dozens of articles on the hydrothermal synthesis of smectite were reviewed (e.g., Kloprogge et al., 1999; Reinholdt et al., 2001, 2005; Lantenois et al., 2008; Andrieux and Petit, 2010; Pascua et al., 2010; Bontognali et al., 2014; Peretyazhko et al., 2016; Golubeva, 2016) before the Taguchi orthogonal array used in this study was designed. The parameters used in the reviewed studies were recorded and statistically analyzed. Subsequently, the most frequently used parameters and levels were selected and integrated into the design of the Taguchi orthogonal array in this study. For a comprehensive consideration, 11 factors were evaluated in this study. At least 34,992 ($3^7 \times 2^4$) experiments would be required for all combinations of the experimental factors if seven of them are three-level factors and four of them are two-level factors. Therefore, the Taguchi method, an efficient experimental design method, was used to optimize the phase purity and yield of the synthetic smectite, and the influence and contribution of synthesis parameters on phase purity and yield are also discussed.

2. Experimental

2.1. Experiment design by Taguchi method

The L18 orthogonal array of the Taguchi method can minimize interactions between experimental factors; therefore, it was adapted in this work as the inner array. This array can contain eight factors, with one two-level factor and seven three-level factors (A to H in Table 1). Eight main factors, including the types of Si, Al, and Mg sources and mineralizers, the amount of mineralizer and excess sodium added, reaction time, and initial pH, were selected for the L18 array. Their levels are shown in Table 2.

Table 2
Inner array for hydrothermally synthesized smectite with eight main factors.

No	Factor	Level 1	Level 2	Level 3
A	Si source	Na_2SiO_3	TEOS	–
B	Mineralizer amount (mL)	0.02	0.025	0.03
C	Reaction time (hours)	48	72	96
D	Initial pH	7	9	11
E	Mineralizer source	HF	NaF	NH_4F
F	Na excess (%)	0	10	20
G	Al source	$Al(NO_3)_3$	$Al(OH)(CH_3COO)_2$	$Al(OH)_3$
H	Mg source	$Mg(NO_3)_2{\cdot}6H_2O$	$Mg(CH_3COO)_2{\cdot}4H_2O$	$Mg(OH)_2$

Table 3
Three noise factors and two levels in the outer array for hydrothermally synthesized smectite.

No	Factor	Level 1	Level 2
α	Reaction temperature	200 °C	220 °C
β	Alkaline solution chemicals	NH_4OH	NaOH
γ	Mg:Al ratio	8:2	9:1

Another L4 orthogonal array was added in this work as the outer array to add another three two-level factors, namely α, β, and γ (Table 3). The reaction temperature, Mg:Al ratio, and chemicals for the alkali solution were selected as noise factors in the L4 outer array. The levels for these three factors are shown in Table 3.

Eighteen sets of experiments were required according to the combinations of different levels for each factor in the L18 array, and four sets of experiments were required for L4. Thus, each set of experiments for L18 included four settings for different conditions of L4. Therefore, a total of 18 × 4 = 72 experiments were performed in this study.

2.2. Synthesis of smectite

Smectite was synthesized under hydrothermal conditions in a steel autoclave with a Teflon container, according to the experimental parameters of each sample shown in Tables 2 and 3. Different

Table 1
L18 as the inner array and L4 as the outer array were used in this study for hydrothermally synthesized smectite.

No	1	2	3	4
α	1	1	2	2
β	1	2	1	2
γ	1	2	2	1

No	A	B	C	D	E	F	G	H	Data 1	Data 2	Data 3	Data 4
1	1	1	1	1	1	1	1	1				
2	1	1	2	2	2	2	2	2				
3	1	1	3	3	3	3	3	3				
4	1	2	1	1	2	2	3	3				
5	1	2	2	2	3	3	1	1				
6	1	2	3	3	1	1	2	2				
7	1	3	1	2	1	3	2	3				
8	1	3	2	3	2	1	3	1				
9	1	3	3	1	3	2	1	2				
10	2	1	1	3	3	2	2	1				
11	2	1	2	1	1	3	3	2				
12	2	1	3	2	2	1	1	3				
13	2	2	1	2	3	1	3	2				
14	2	2	2	3	1	2	1	3				
15	2	2	3	1	2	3	2	1				
16	2	3	1	3	2	3	1	2				
17	2	3	2	1	3	1	2	3				
18	2	3	3	2	1	2	3	1				

8 main factors of L18 array
3 factors of L4 array
4 sets of experiments for L4 array
Levels of 3 factors for each experiment in L4 array
18 sets of experiments for L18 array
Totally 72 (18*4) experiments need to be run
Levels of 8 factors for each experiment in L18 array