Chapter 7
Clay Minerals Converted to Porous Materials and Their Application:
Challenge and Perspective

Pham Thanh Huyen
Hanoi University of Science and Technology, Vietnam

ABSTRACT

Clay minerals can be used as raw materials for the production of various industrial products. However, most bentonite and kaolinite deposits contain a significant quantity of non-clay mineral impurities. These impurities often affect the quality of clay minerals for adsorption and catalytic application. Therefore, in order to be used as adsorbents and catalysts, those clay minerals need some beneficiation, activation processing to improve their properties or conversion to a porous materials. In this chapter, an overview of the current state, the properties, the beneficiation, activation as well as the conversion of bentonite, kaolinite… to porous materials such as pillared clays, zeolites and their intended applications were presented. In addition, in this review, the challenges and difficulty in the conversion of bentonite and kaolinite to porous materials were also discussed.

INTRODUCTION

Clays have attracted great attention for sustainable materials or environmental materials. Clay minerals such as bentonite and kaolinite have characteristics of high surface area, layered structure, chemical and mechanical stability, cation exchange ability, abundant in nature and low cost and can be used for many industrial applications. The structure and composition of these clays usually influence their physical and chemical properties and determine the applications of the clay minerals *(Muray, 1991)*. Industrial uses of bentonite depend on quality and quantity of their smectites (especially montmorillonite content), as well as the type, valence and the amount of exchangeable cations *(Önal & Sarikaya, 2007)*. Most bentonite contains a significant quantity of non-clay mineral impurities or other clay minerals, therefore,

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bentonite needs some beneficiation to the activation processing to improve their properties or conversion to a porous materials.

In order to increase the surface area and acidity of the clay minerals, as well as eliminate several mineral impurities, acid treatment process is needed. Treatments of clay minerals with inorganic acids of rather high concentration and usually at high temperature are known as acid activation. The acid treatment changes surface area and porous structure of the clays. Key parameters which influence the acid treatment process are: the present of other clay minerals and non-clay minerals, the chemical composition, the type of cations between the layers, the type of the acid, the activating temperature and time, acid to bentonite ratio and so on *(Nguetnkam, Kamga, Villiéras, Ekodeck, Razafitianamaharavo, & Yvon, 2005;Bhattacharyya & Gupta, 2008;Amari, Chlendi, Gannouni, & Bellagi, 2010)*. However at high acid concentration, aluminum component in the framework can also be dissolved and leads to the collapse of the clay structure, resulting in the decrease of the surface area. So the activation reaction condition should vary depending on the treatment condition. The cations between the layers of montmorillonite could be exchanged with large polyoxocations which is then converted to oxide clusters upon calcination to form pillared clays. Zeolites are crystalline aluminosilicates that have uniform microporous system. Therefore this kind of clays can be used as adsorbents or catalyst supports. Most research papers described zeolites synthesized from pure and expensive chemicals containing organic aluminum and silicium (such as aluminum isopropoxide, tetraethyl orthosilicate TEOS) and organic templates (tetramethylammonium hydroxide TMAOH, tetramethylammonium bromide TMABr and so on) in alkaline media on certain conditions *(Don, Huyen, Hong, 2013).* Recently, kaolinite-based zeolites are reported using cheap natural materials compared to conventional system which are therefore more cost efficient (*Johnson & Arshad, 2014).*

Background

Bentonite is composed mostly of montmorillonite which are made up of two silica tetrahedral sheets with a central alumina octahedral sheet. The tetrahedral and octahedral sheets are combined in such way that the tips of the tetrahedra of and one of the hydroxyl layers of the octahedral sheet form a common layer (Figure 1). The atoms in this layer, which are shared to both sheets, become oxygen instead of hydroxyl.

In order to create porous structure and increase the surface area and acidity of the clay minerals, as well as eliminate the mineral impurities, inorganic acids such as H_2SO_4, HCl *(Pawar, Lalhmunsiama, Bajaj & Lee, 2016)*, HNO_3*(Ishaq, Sultan, Ahmad, Ullah, Yaseen, & Amir,, 2015)* can be used. However, up to now, few work using HNO_3 has been reported.

An alternative way to use clays as a porous materials is pillared clays. Pillared clays (PILCs) are layered materials, prepared by substituting the small mono and divalent interlayered cations in the smectite layers, with large polyoxocations or charged colloidal particles. Upon heating, the cationic pillars form oxide clusters that insert between the clay layers, creating a well defined two-dimensional pore structure with high specific surface area (*Lenarda, Ganzerla, Storaro, Enzo, & Zanoni, 1994;Gandia, Vicente, & Gil, 2000;Bineesh, Kim, Kim, & Park, 2011).* The cross-linking of oligocations to the clay layers creates a stable texture, which supply the solid with a developed network of micro- and mesopores. PILCs have high acidity, which is due to the parent materials and to the exchangeable cations, an oxyhydroxide that provides Brönsted and Lewis acidity, which is easily tunable by changing the synthesis conditions *(Kou, Mendioroz, Salerno, & Muñoz, 2003).* Therefore PILCs have been used as supports and bifuntional catalysts *(Gil, Korili, Trujillano, & Vicente, 2011*).

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