



## Research paper

## Structural features and stability of Spanish sepiolite as a potential catalyst

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## ABSTRACT

Sepiolite-based catalysts loaded with potassium hydroxide were prepared via the wet impregnation and ion-exchange methods and evaluated as catalysts in base-assisted reactions, such as transesterification of renewable oils. The structural features of these catalysts were characterised in detail by variable-temperature in situ X-ray diffraction, N<sub>2</sub> adsorption-desorption, scanning electron microscopy with energy-dispersive X-ray analysis and in situ FTIR spectroscopy. Although a high yield of fatty acid methyl esters was achieved in transesterification reactions in the presence of K-containing sepiolite, this system showed significant deactivation due to its structural degradation and loss of the active component during the reaction and regeneration cycles. This work demonstrates for the first time how the thermal and structural stability of sepiolite based systems can affect their performance, which is an essential issue that has not been sufficiently addressed in recent research related to the catalytic applications of these materials.

## 1. Introduction

Nanoporous materials have been used in a host of catalytic applications owing to their versatile pore networks, enhanced reactivity, stability, chemical functionality and high surface area (Corma et al., 2006; Somorjai and Na, 2015; Mota et al., 2016). Many studies have illustrated the use of alkaline, alkaline earth and transition metal oxides supported on nanoporous materials with the pore size of ~1–100 nm, such as silicas, clays and zeolites prepared by impregnation, ion exchange and precipitation as highly active catalysts (Corma and Martin-Aranda, 1991; Gedanken et al., 2016). One of the processes for the production of an environmentally friendly fuel from vegetable oils and animal fats is the transesterification reaction between triglycerides (TGs) in oils or fats and an alcohol, which is carried out in the presence of an acid or base catalyst yielding fatty acid methyl esters (FAMES) and glycerol. For this reaction, heterogeneous catalysis can offer a greener route with potential advantages including the elimination of the quenching step, separation of the products and associated aqueous waste (Gandía et al., 2018).

Sepiolite (Sep), often in close association and intergrowth with palygorskite, is known from many localities worldwide but is typically found in only small amount compared to other minerals that form under similar geological conditions. The low specific gravity, high porosity and capacity to float on water led to the original name “Meerschaum” (German for “foam of the sea”) by Abraham Gottlob Werner. Later, based on its similarity with cuttlebone, the internal shell

of cuttlefish, the name “sepiolite” from Greek “sepiion” (cuttlebone) and “lithos” (stone) was given to the mineral for a find in the Piedmont region of Italy. Sep requires alkaline conditions, with high activities of silicon and magnesium (Singer, 1989), and is also often associated with low latitudes and arid to semi-arid climates. Environments of formation include marine, lacustrine and lagoonal continental sediments, soils, palaeosols and calcretes (Deer et al., 1992). Replacement of pre-existing minerals such as magnesite (Yeniyoğlu, 1986), hydrothermal alteration (e.g. Ehlmann et al., 1962; Irkeç and Unlu, 1993) and a role of biomineralisation (e.g. Leguey et al., 2010) have also been suggested for the formation of Sep. Large, economically valuable Sep deposits originate mostly from formation in shallow seas and lakes as chemical sediments. At Eskişehir (Turkey), the richest Sep mining field in the world, Sep occurs as layers and nodules in Neogene lacustrine sediments (Kadir et al., 2016). Other notable Sep occurrences are in the United States, the Czech Republic, Greece, France and Spain. The latter includes Sep-rich deposits in southern and central Spain associated with lagoonal and lacustrine environments (e.g. Galán and Ferrero, 1982; Galán and Castillo, 1984; Torres-Ruiz et al., 1994; Armenteros et al., 1995; Bustillo and Alonso-Zarza, 2007).

Together with palygorskite, Sep is a member of the palygorskite group of clay minerals, which belong to the sheet silicate (phyllosilicate) group of the silicates (Deer et al., 1992). These minerals are characterised by the same basic building blocks, namely a tetrahedral sheet and one of two kinds of octahedral sheets, combined to form composite mineral structures. In contrast to other sheet silicates, Sep, a

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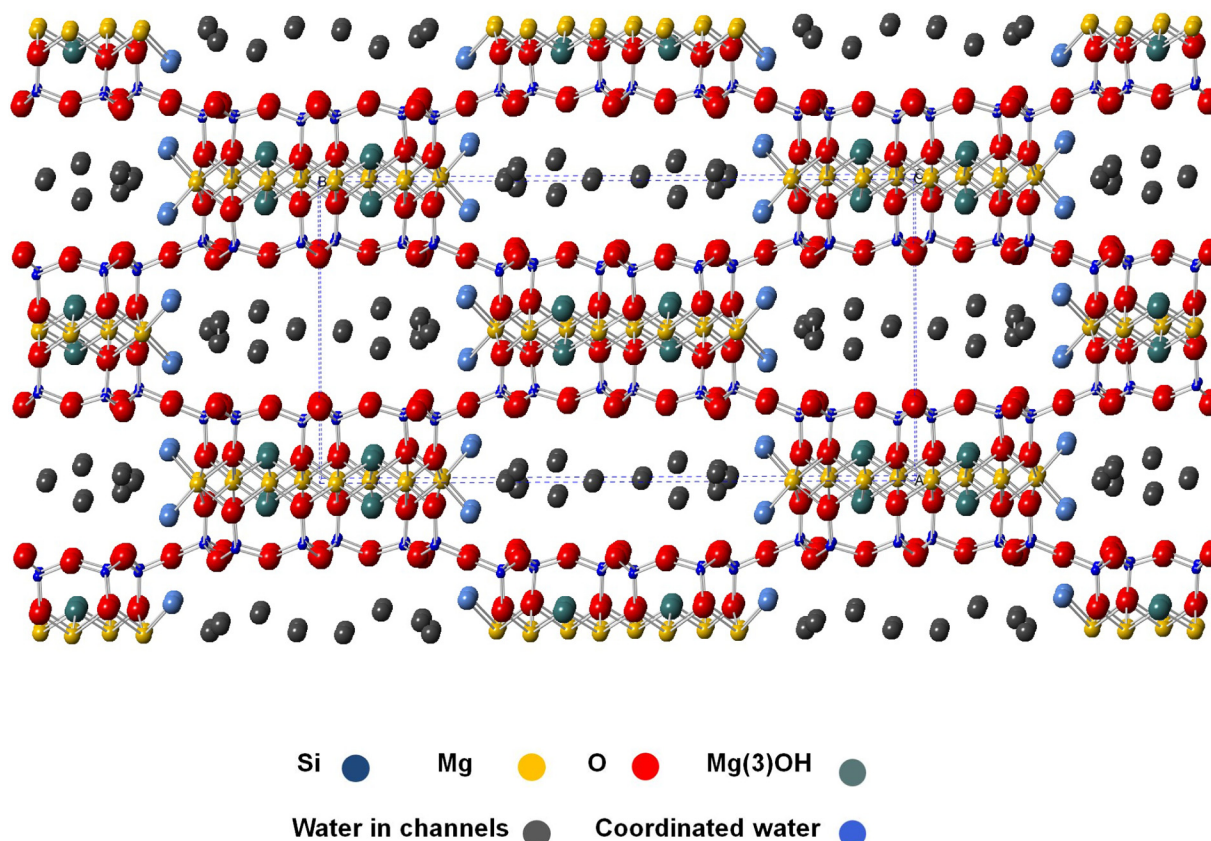


Fig. 1. Sepiolite structure (the blue dotted line indicates the unit cell size). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

fibrous hydrated magnesium silicate with the ideal chemical formula  $\text{Mg}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$  (the formula  $\text{Mg}_8\text{Si}_{12}\text{O}_{30}(\text{OH})_4 \cdot 4(\text{H}_2\text{O}) \cdot n\text{H}_2\text{O}$  is also used in the literature), lacks continuous octahedral sheets (Fig. 1). The tetrahedral sheets are continuous; however, ribbons rather than sheets of octahedra leave channels ( $0.36 \times 1.06$  nm in size) in the Sep structure that can accommodate water and organic molecules (Deer et al., 1992). Furthermore, Sep is characterised by a high specific surface area and good surface affinity toward organic and inorganic species (Kadir and Akbutut, 2003; Sabah and Çelik, 2005; Suarez et al., 2016).

There has been a great deal of interest in utilising the sorptive, rheological and catalytic properties of Sep in many industrial applications (Alvarez, 1984). For instance, Sep has been recently used as catalyst support for green chemistry applications (Figen et al., 2018). Furthermore, a number of studies have been focused on the applications of natural clay minerals including Sep, red mud and bentonite as catalysts for the production of renewable fuels. Alves et al. (2014) utilised treated smectite clay with potassium fluoride in transesterification of soybean oil utilising the clay as a solid catalyst. Soetaredjo et al. (2011) examined the performance of potassium hydroxide impregnated bentonite as a catalyst for palm oil conversion. Agustian et al. (2012) used three metal (Ba, K and Na) hydroxides supported on bentonite as catalysts for methanolysis of *Jatropha curcas* oil. Degirmenbasi et al. (2014) used  $\text{K}_2\text{CO}_3$  loaded Sep as a solid catalyst in transesterification of canola oil. Xu et al. (2013) employed red mud containing strongly basic active sites on the surface as a catalyst for biodiesel production from soybean oil. Most authors reported a high yield of FAMES, typically over 90%, after several hours of the reaction time at temperatures above  $65^\circ\text{C}$ .

Important problems for heterogeneous systems, which can affect the catalytic performance, are structural integrity, thermal stability and the loss of active phases from the catalyst. A considerable challenge in an

industrial application is maintaining the high catalyst activity for a number of reaction and regeneration cycles. However, many published reports do not describe the structural characterisation of the clay based catalysts before and after the reaction studies, which are often limited to a very small number, if any, of the successive runs on regenerated catalysts.

In this paper, potassium hydroxide loaded Spanish Sep has been prepared via wet impregnation and ion-exchange, and then used for the production of biofuel from both non-edible and edible oils using microwave heating. The aim of the present study is twofold: to carry out a detailed structural characterisation of the Sep-based catalyst both before and after the reaction and to evaluate the structure - performance relationship in the transesterification reaction for the production of biofuel from renewable feedstock for sustainable and clean energy applications.

## 2. Experimental

The Spanish Sep (ACS reagent) was obtained from Sigma-Aldrich. Potassium hydroxide (86%), methanol, sodium hydroxide (99%) and n-heptane (analytical grade, > 99.99%) were purchased from Fisher Scientific. The grapeseed oil was supplied by Now Solutions (USA), refined rapeseed oil was purchased from a local market and castor oil was obtained from Fisher Scientific. Methyl heptadecanoate (analytical GC standard, > 99.99%) was supplied by Sigma-Aldrich.

Two types of catalysts were prepared by impregnation (K-Sep-Imp) and ion-exchange (K-Sep-IE) procedures. These were characterised before and after the reaction using in situ variable-temperature X-ray diffraction (VT XRD), scanning electronic microscopy with energy-dispersive X-ray analysis (SEM-EDX), thermogravimetric analysis (TGA), nitrogen adsorption-desorption and in situ FTIR spectroscopy. Detailed procedures are provided in the Electronic Supplementary Material

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