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_2 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.

Keywords:

Structural stability, in situ XRD, Sepiolite, Transesterification, Microwave Catalysis

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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 ñMeerschaumò (German for ñfoam of the seaò) by Abraham Gottlob Werner. Later, based on its similarity with cuttlebone, the internal shell of cuttlefish, the name ñsepioliteò from Greek ñsepionò (cuttlebone) and ñlithosò (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 (Yeniyol, 1986), hydrothermal alteration (e.g. Ehlmann et al., 1962; Irkeç and Ünlü, 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 Eskiкehir (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-Ruíz 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 fibrous hydrated magnesium silicate with the ideal chemical formula $Mg_4Si_6O_{15}(OH)_2 \cdot 6H_2O$ (the formula $Mg_8Si_{12}O_{30}(OH)_4 \cdot 4(H_2O) \cdot nH_2O$ is also used in the literature), lacks continuous octahedral sheets (Figure 1). The tetrahedral sheets are continuous; however, ribbons rather than sheets of octahedra leave channels (0.36×1.06 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 towards organic and inorganic species (Kadir and Akbulut, 2003; Sabah and Çelik, 2005; Suarez et al., 2016).

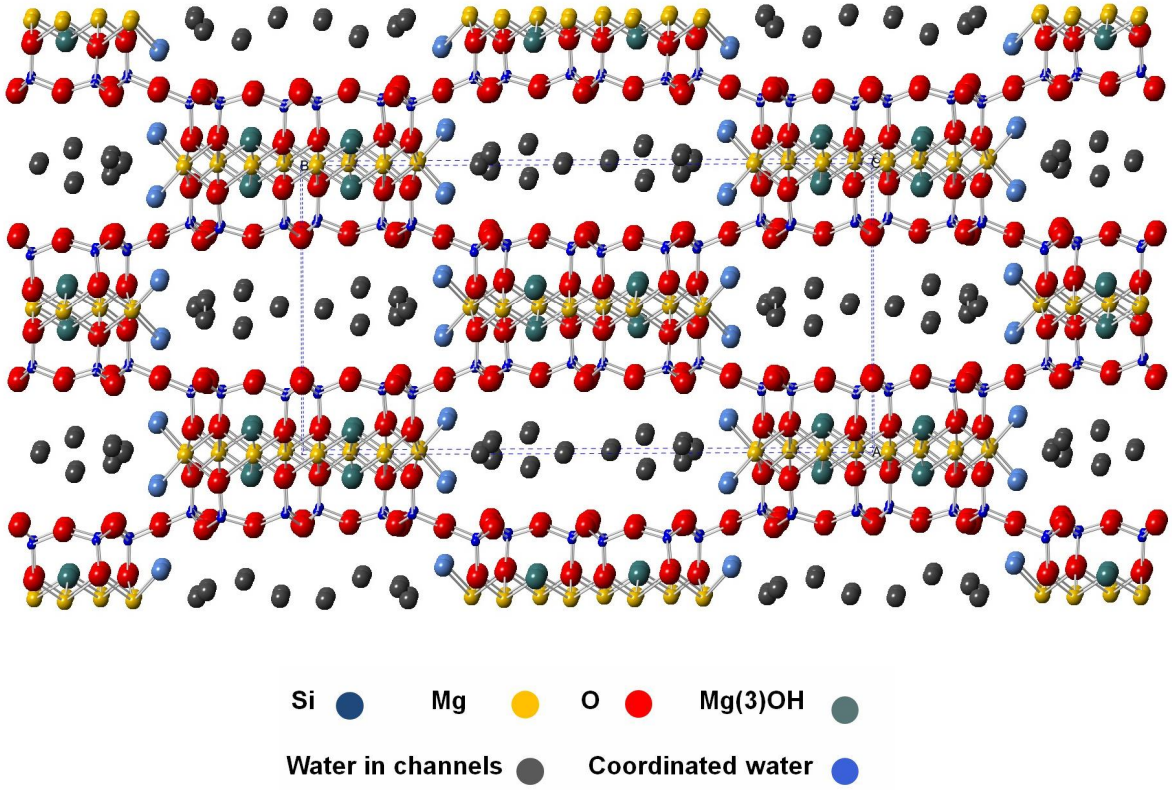


Fig. 1. Sepiolite structure (the blue dotted line indicates the unit cell size).

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. Agustain 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 K_2CO_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°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 (ESM).

Following the transesterification reaction (Figure S1), the catalysts were separated, rinsed with methanol, dried at 60^{o}C and reactivated under the same conditions as prior to the initial reaction and utilised again. The same reaction conditions were used in four consecutive runs for the recycled catalysts.

3. Results and discussion

One of the most important characteristics of a working catalyst is its structural stability. This can be affected at different stages of the catalyst activation and regeneration or in the course of the reaction itself. The structural properties of the Sep-based catalysts were monitored by both in situ and ex situ XRD, FTIR and N_2 adsorption. Figures 2 and S2 (ESM) present the VT-XRD patterns of the Sep and K-Sep-Imp recorded at different calcination temperatures. There are clear changes in the patterns of both materials recorded above 200^{o}C. For Sep in particular, the intensity of the 110 reflection at 7.48^{o} (1.18 nm d-value; a summary of the indexed XRD reflections is given in Table S2), which corresponds to the interlayer distance in the clay structure, decreased significantly, becoming negligible above 300^{o}C. Similar intensity changes were observed for the same reflection (1.19 nm d-value) in the patterns of the K-Sep-Imp sample. It is suggested that the layered structure of the catalyst collapsed during the high temperature calcination. The observed structural changes are not reversible as the VT-XRD patterns, recorded for both materials upon cooling, did not change. Our data are in accord with the findings of Preisinger (1959), Dany and Nadiye-Tabbiruka (1975) and Grillet et al. (1988) indicating that the Sep structure showed significant changes upon heating above 150^{o}C, which was accompanied by the loss of water and microporosity. In addition, an in situ variable-temperature synchrotron investigation (Post et al., 2007) and a number of ex situ studies (Kok, 2013; Pıkkin, 2013; Yeniyol et al., 2014) on Sep samples calcined up to 900^{o}C demonstrated the folding of the Sep structure resulting from its dehydration above 320^{o}C with the loss of the micropore channels, which was followed by the formation of two "anhydrous" Sep phases at ~460 and 650^{o}C. These results and most literature data, however, disagree with those presented by Degirmenbasi et al. (2014), who suggested that heating Sep to 500^{o}C did not cause any change in the catalyst structure. Our nitrogen adsorption and TGA-DSC data support the VT-XRD finding. Indeed, the BET surface area (S_{BET}) of Sep decreased with increasing activation temperature from 325 to 130 m^2/g (Figures 3, 4 and S3, ESM); the BET surface area of K-Sep-Imp was below 100 m^2/g. Therefore nitrogen adsorption and XRD data clearly demonstrate that potassium introduction and activation at elevated temperatures lead to considerable structural degradation and a significant decrease in the S_{BET}. In addition, the micropores present in the original Sep (~0.8 nm in diameter) in the spaces between the silicate layers were no longer detected for the samples activated at temperatures above 200^{o}C. These results are also supported by previous research (Gómez-Avilés et

al., 2013; Pikkin et al., 2013; Pozo et al., 2014; Suarez et al., 2016). While these publications did confirm the high surface area of Sep and indicate the presence of micropores, to the best of our knowledge, our work is the first to present a detailed characterisation of a series of thermally treated Sep samples in the region of low P/P_o values corresponding to the micropore filling by nitrogen.

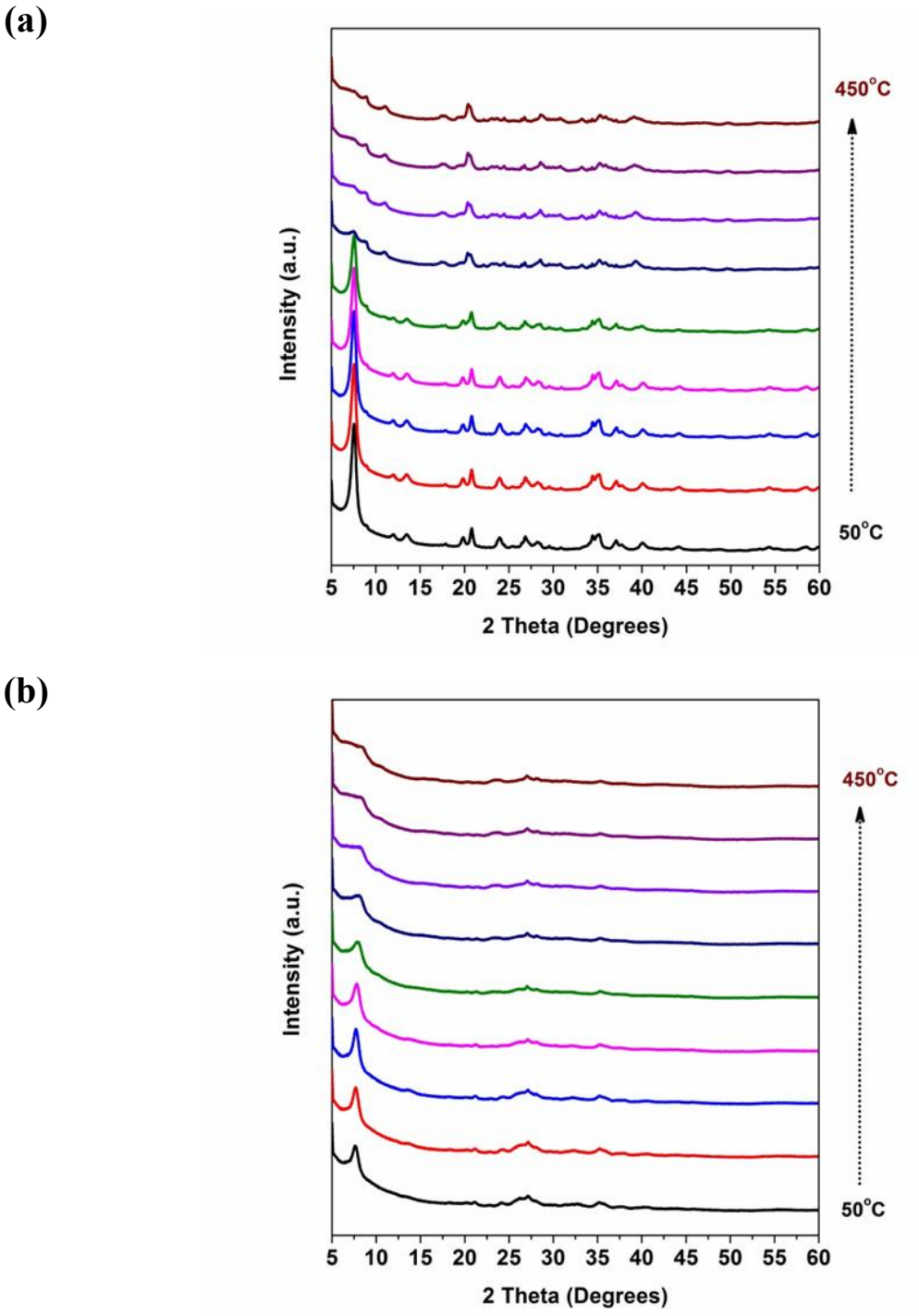
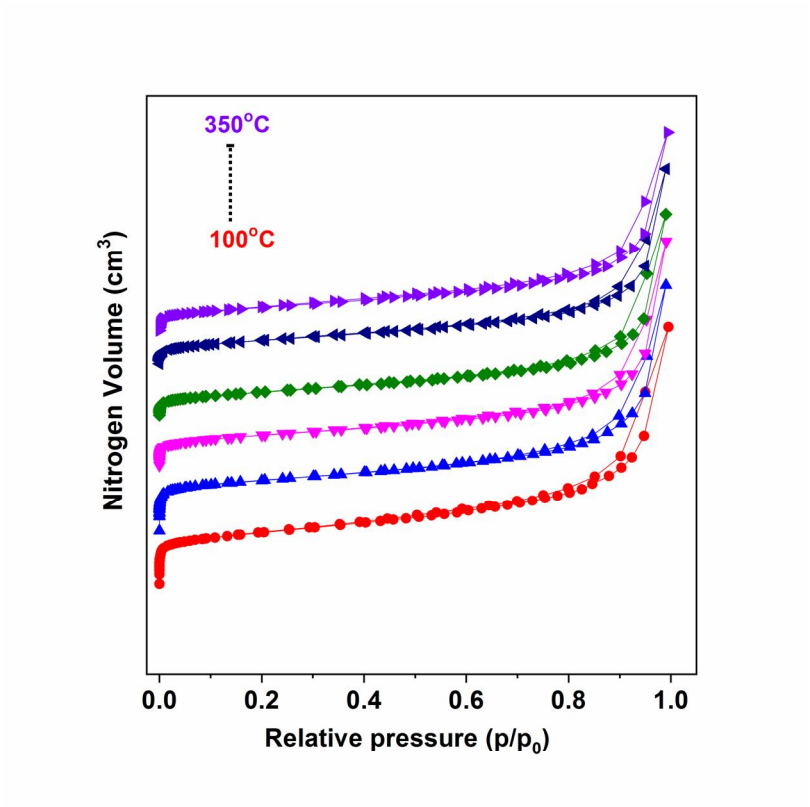


Fig. 2. In situ VT XRD patterns collected every 50°C (heating up) of (a) parent Sep catalyst and (b) K-Sep-Imp. Patterns are offset for clarity.

(a)



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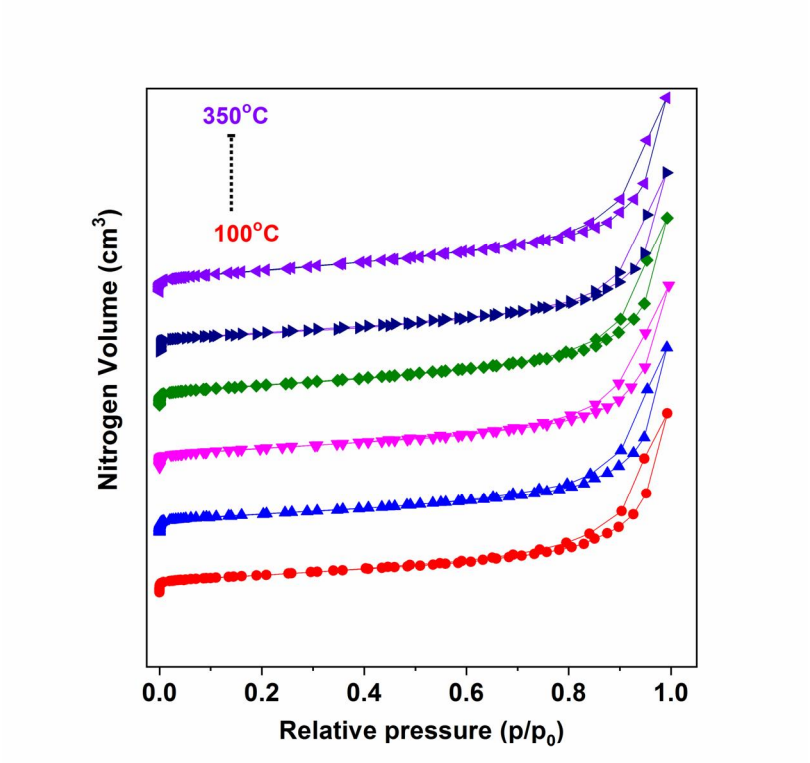

Fig. 3. Nitrogen adsorption isotherms for (a) Sep and (b) K-Sep-Imp activated at 100-350°C in 50°C steps. Isotherm traces are offset for clarity.

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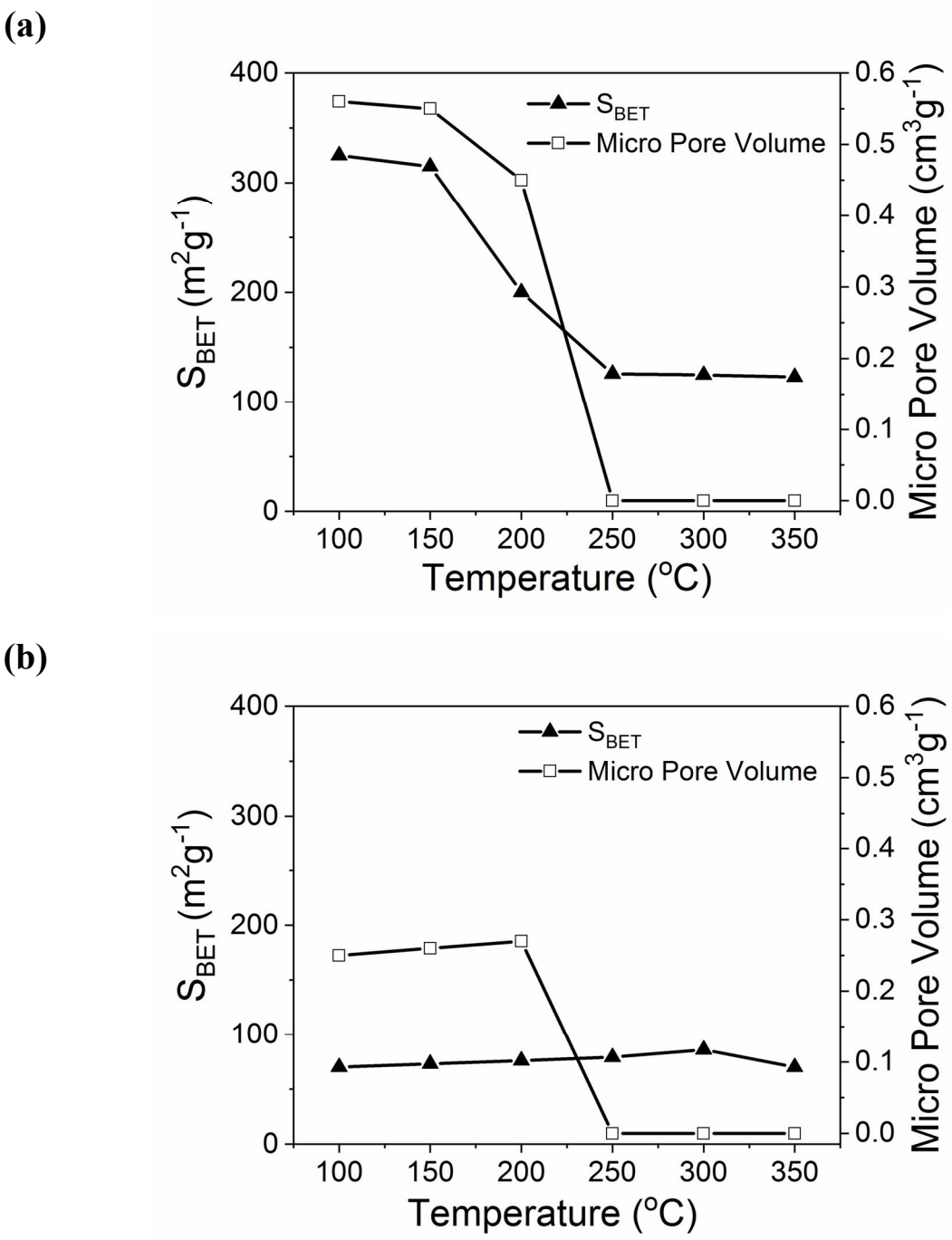


Fig. 4. Specific surface area and micropore volume data as a function of the activation temperature for (a) Sep and (b) K-Sep-Imp.

Although the thermal treatment process is essential for the decomposition of the metal precursor, there is a significant change in the catalyst properties caused by heating above 250°C, which is associated with the loss of water and the collapse of the layered structure. In agreement with previous studies (Hayashi et al., 1969; Kok, 2013; Ogorodova et al., 2016), our TGA-DSC data confirmed the stepwise removal of water from Sep, which accounts for ~9% of the mass loss at 100°C and ~4% at 250-300°C (both steps are endothermic processes as expected) with the total mass

loss of ~18% by 900°C (Figure 5). The exothermic peak observed at 850°C corresponds to a high temperature phase transition resulting in a complete loss of the Sep structure. The data obtained for K-Sep were largely similar, ~15% of the mass loss at 400°C and ~18% by 900°C, but showing a more gradual removal of water from this material as compared to the parent Sep sample (Hayashi et al.,1969).

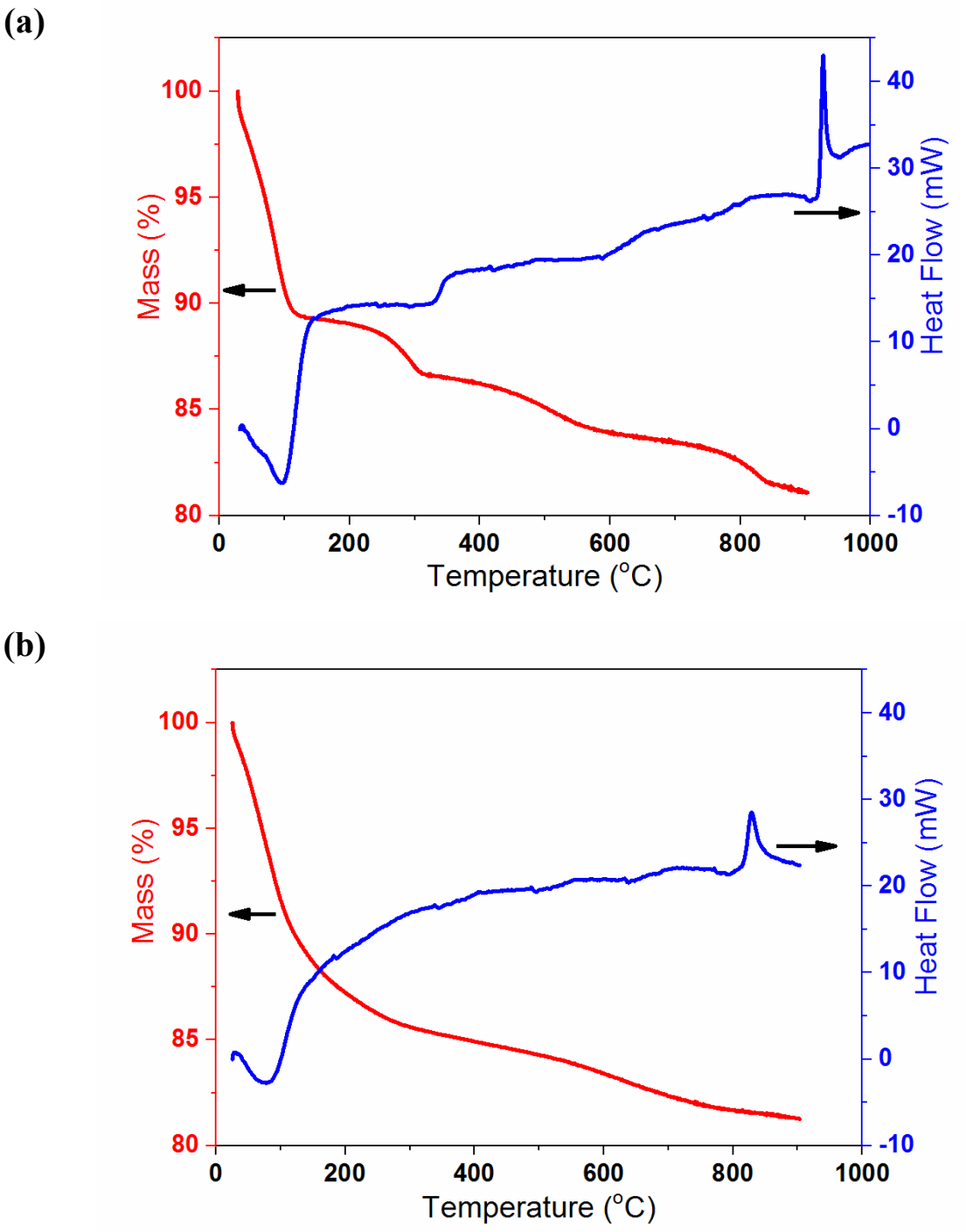


Fig. 5. Thermogravimetric analysis data for (a) Sep and (b) K-Sep.

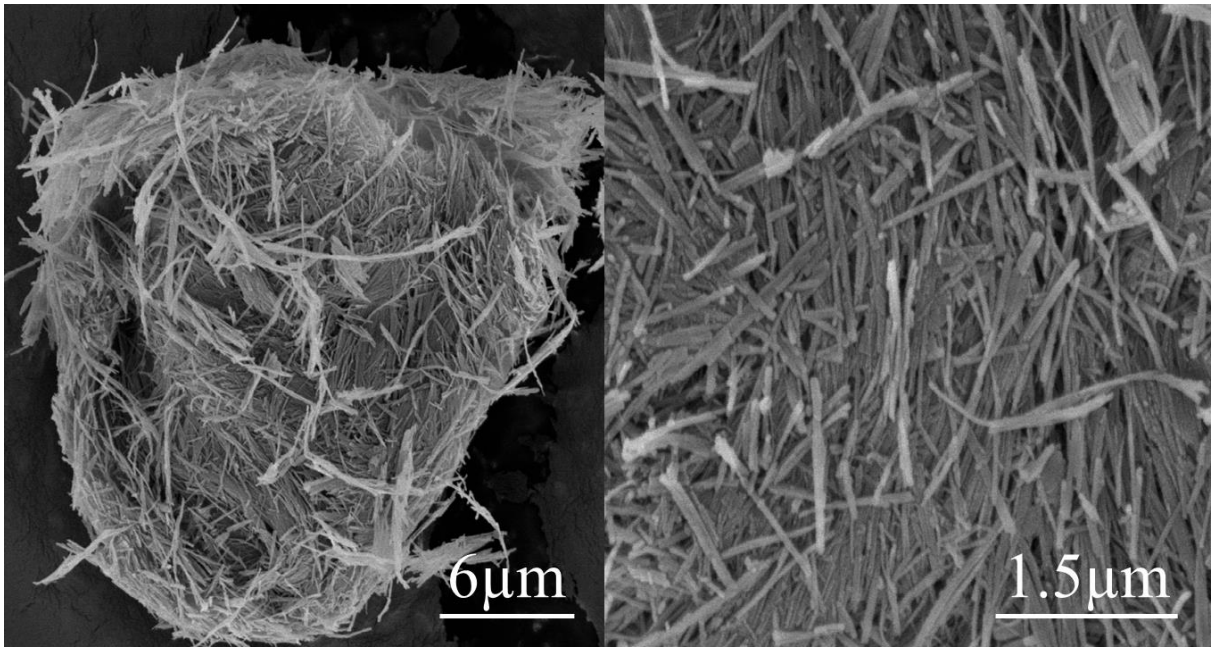
Chemical analysis data and SEM images for Sep, K-Sep-Imp and used K-Sep-Imp are presented in Table 1 and Figure 6, respectively. The chemical analysis results correspond to the empirical formula $2MgO{\cdot}3SiO_2{\cdot}nH_2O$ of the original sample. The potassium content of 6.1 wt% in K-Sep indicates ~60% efficiency of the impregnation procedure. The potassium concentration decreased significantly after the reaction-regeneration cycle, whereas there were no changes to the morphology of K-Sep-Imp and used K-Sep-Imp, which would have implications for the catalytic performance of these materials. Table 1 also summarises the S_{BET} values obtained for the studied Sep based catalysts Interestingly, the nitrogen adsorption data show that the specific surface area of used K-Sep catalysts did not change noticeably after the reaction-regeneration cycle being in the region of ~80 m^2/g, but the micropore volume decreased significantly, which is probably due to the micropore blockage by the reacting species that could not be removed under the relatively mild regeneration conditions. A greater reduction in the S_{BET} may be expected due to the loss of micropores in the used catalysts, however, this is probably compensated by the removal of the K-containing species from the external surface (see below).

Table 1. Elemental analysis and nitrogen adsorption data for Sep based catalysts.

Material	***Elemental composition (wt %)***				***S_{BET} (m^2/g) [a]***	***V_{micro} (cm^3/g) [a]***
	Silicon	***Magnesium***	***Potassium***	***Sodium***		
Parent Sep	22.5	13.3	<0.2	-	195	0.39
K-Sep-Imp	17.3	13.4	6.1	-	75	0.27
K-Sep-Imp used	17.2	13.3	3.2	-	70	0.01
K-Sep-IE	19.7	11.8	4.0	4.6	85	0.28
K-Sep-IE used	19.8	12.0	2.5	1.8	80	0.01

[a] All materials were activated at 200°C.

(a)



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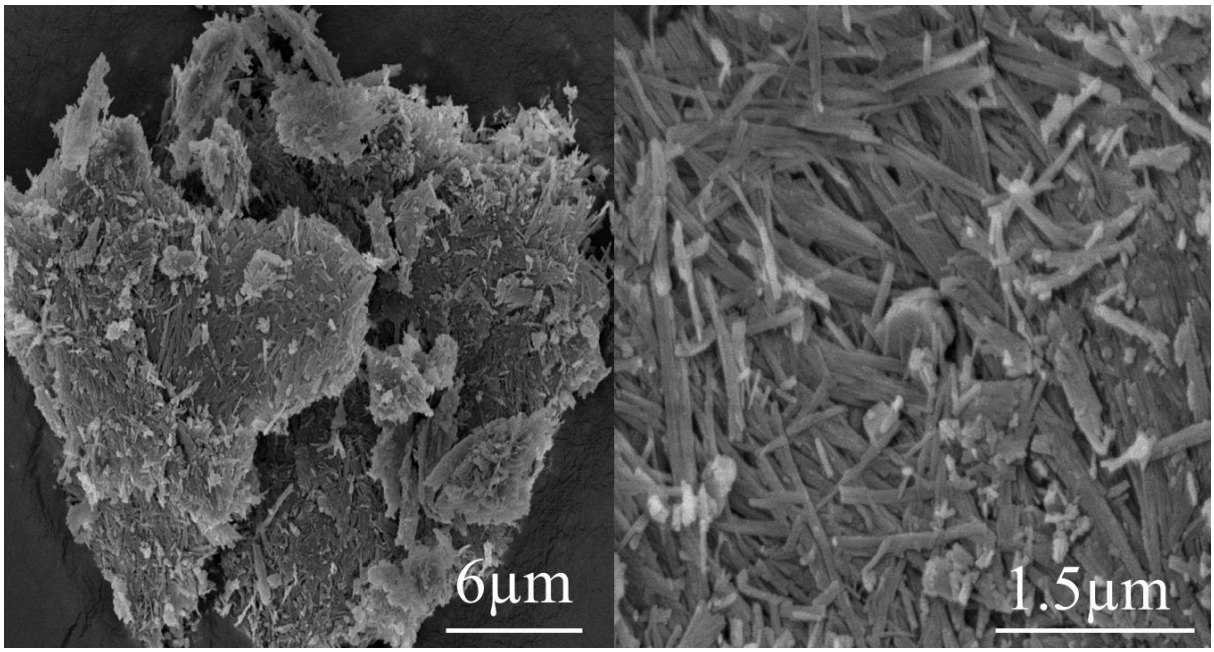

(c)

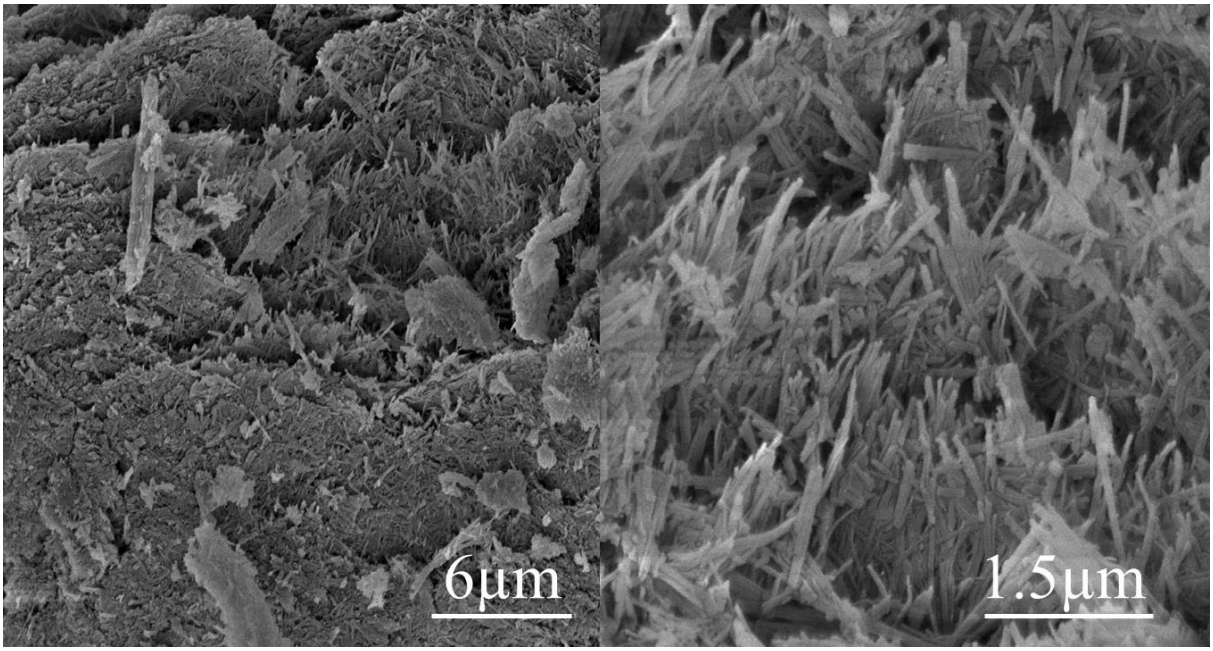

Fig. 6. SEM images of (a) Sep, (b) K-Sep-Imp and (c) K-Sep-Imp following reaction and regeneration.

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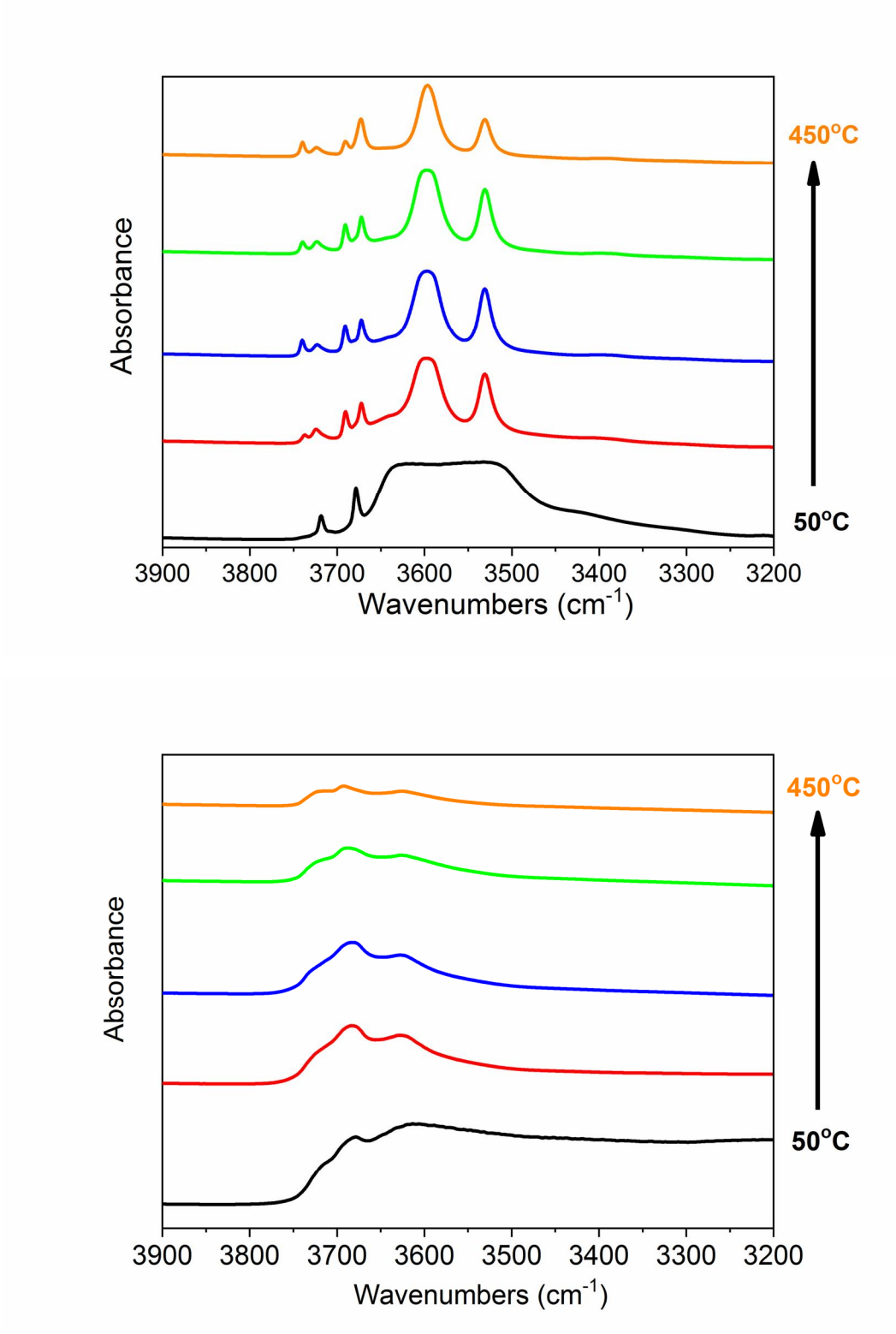

Fig. 7. The OH-region of FTIR spectra for (a) Sep and (b) K-Sep-Imp catalysts activated at 50-450°C in 100°C steps. Spectra are offset for clarity.

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The OH region of the FTIR spectra for Sep and K-Sep-Imp are presented in Figure 7 (the wide range spectra, from 1000 to 6000 cm^{-1} including the overtones and combination frequencies, are available in ESM, Figure S4). The evolution of the spectral bands of different types of OH groups was followed in situ during sample dehydration between 30 and 450^{o}C. The initial spectra were dominated by the broad feature at ~3650-3300 cm^{-1} owing to weakly bound water molecules, which are commonly referred to as "zeolitic water" in the mineralogical literature, and which were removed upon mild dehydration at 150^{o}C. Two overlapping bands at 1625 and 1616 cm^{-1} were also observed in the region of OH-bending vibrations. The spectra of the dehydrated samples exhibited six peaks in the region of stretching O-H vibrations. In agreement with the literature (Hayashi et al., 1969; Frost et al., 2001; Ruiz et al., 2010; Giustetto et al., 2010; Bukas et al., 2013; Post et al., 2014; Chryssikos et al., 2015), the peaks at 3740 and 3724 cm^{-1} are assigned to Si-OH groups of the tetrahedral silicate layer and those at 3691 and 3673 cm^{-1} to Mg(3)-OH groups in the octahedral sheets of the Sep structure. The bands at 3597 and 3531 cm^{-1} are attributed to water molecules coordinated to Mg cations, which is supported by the presence of a single band at 1616 cm^{-1} in the region of bending OH vibrations. Interestingly, these peaks persisted in the spectra of the samples dehydrated in vacuum at 450^{o}C for 5 hours. It should be noted that there are minor variations in the position of the absorption bands reported in the literature, which is probably related to the fact that most of the previous data were obtained using ex situ experiments on calcined samples or KBr disks with somewhat uncertain degree of control over the hydration and dehydration processes. Although the interpretation of the spectra has been supported by extensive NIR characterisation of Sep (Frost et al., 2001; Ruiz et al., 2010; Giustetto et al., 2010; Chryssikos et al., 2015), a different assignment could not be completely ruled out. For instance, two OH bands at 3734 and 3583 cm^{-1} were observed in the spectra of magnesium oxide calcined at 500^{o}C (Hadjiivanov, 2014). The spectra of K-Sep dehydrated at elevated temperatures displayed rather broad overlapping bands between 3750 and 3600 cm^{-1}. This is in agreement with our VT-XRD and nitrogen adsorption data indicating considerable structural degradation upon KOH impregnation and calcination of this material.

The structural stability, high surface area and strong bonding with the active phase preventing the loss of the active sites are essential characteristics of a supported catalyst (Romero et al, 2016). Figure 8 presents a comparison of the catalytic performance of K-Sep-Imp in transesterification of triglycerides over several reactions ï regeneration cycles. These data demonstrate a significant deactivation of K-Sep-Imp, which can be linked to its structural integrity and loss of the active sites. Although we obtained high yield and selectivity of FAMEs in the presence of K-Sep-Imp and K-Sep-IE, these materials lack long-term stability in the methanolysis reaction. A considerable change

in the catalyst structure was found after calcination at elevated temperatures, accompanied by the loss of water and a significant reduction in its surface area. In contrast to our results and the data available in the literature, Degirmenbasi et al. (2014) concluded that a higher catalytic activity of Sep impregnated with K_2CO_3 in the transesterification of canola oil is achieved following its calcination to 500^{o}C, apparently resulting in a catalyst more resistant toward the leaching of the active phase. However, our structural characterisation, chemical analysis and catalytic data for the Sep-based catalysts that were calcined or regenerated at temperatures between 250 and 450^{o}C provide no evidence of enhanced catalytic performance or improved structural stability following the high temperature treatment. In addition, characterisation of the regenerated catalysts demonstrated that the K^+ ions were leaching out during the transesterification reaction or the regeneration step, which was accompanied with a significant drop in the yield of FAMEs in the subsequent catalytic run from 100% to 78%. A similar drop in activity was observed for the K-Sep-IE.

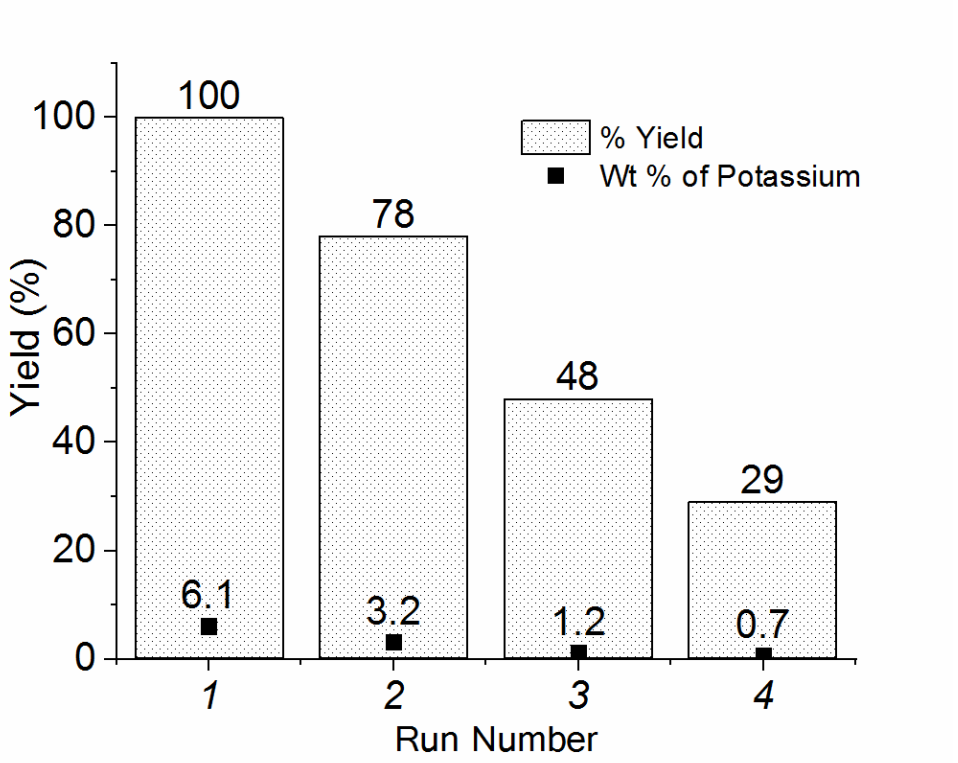

Fig. 8. Catalytic performance of the fresh and used K-Sep-Imp in the transesterification of grapeseed oil at 160^{o}C and the wt% of potassium in these catalysts**.**

Furthermore, in a blank reaction run with 0.0035g of KOH (approximately the amount of potassium hydroxide lost by K-Sep-Imp in the first reaction cycle), a triglyceride conversion of ~75% was observed, confirming that potassium hydroxide in solution was active in the transesterification reaction. Clearly, such effects should be taken into account, considering a significant number of

studies utilising clay-based catalysts either impregnated or ion-exchanged with potassium containing compounds (Corma and Martin-Aranda, 1991; Villamiel et al., 2002; Ilgen and Akin, 2012; Degirmenbasi et al., 2013, 2014; Chryssikos et al., 2015; Wang et al., 2017).

4. Conclusion

The application of heterogeneous catalysts in the production of biodiesel offers potential advantages including lower cost, high stability and the ease of separation. In this work, Sep modified with K-bearing compounds was prepared using impregnation and ion exchange procedures. The evolution of the structural features of these catalysts was characterised in detail both before and after the reaction by variable-temperature in situ XRD, N_2 adsorption-desorption, SEM-EDX and in situ FTIR spectroscopy in order to evaluate their structure - performance relationship in the methanolysis of vegetable oils. Our data demonstrated that the Sep structure undergoes irreversible changes upon heating above 250^{o}C, which are accompanied by the loss of water and OH groups. High-temperature calcination resulted in dehydration of Sep followed by the folding of its structure with the loss of the micropore channels and significant decrease in the surface area. Sep impregnation with KOH also led to partial structural degradation and decrease in the surface area. Subsequent thermal treatment, required for the decomposition of the metal precursor with the formation of an oxide on the Sep support, can cause further structural changes associated with dehydration and the collapse of the layered structure. Although high yield of FAMEs was obtained in transesterification in the presence of K-Sep, our work demonstrated that both impregnated and ion-exchanged K-Sep lack long-term stability in this reaction due to the loss of the active component during the recycling stages. Overall, our reaction studies and extensive structural analysis point to a potentially significant contribution of the homogeneously catalysed transformation of triglycerides in the presence of clay-based catalysts.

Acknowledgments

This work was supported by Ministry of Oil /Oil Marketing Company (SOMO), Baghdad, Iraq under grant SL-144-01B. The authors appreciate the support of the Lennard-Jones Laboratories and the School of Geography, Geology and the Environment at Keele University, UK, where this study was carried out. We thank Karen Walker of Keele University for her help with obtaining SEM images.

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