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Sustainable conversion of waste corn oil into biofuel over different forms of synthetic muscovite based K⁺/Na⁺ sodalite as basic catalysts; characterization and mechanism

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Abstract

Novel types of sodalite enriched in both K⁺ and Na⁺ ions were synthesized from muscovite at different time intervals (24 h (SD-24), 48 (SD-48), and 72 h (SD-72)). The samples displayed changes in their morphologies and observable increment in the surface area, total basicity, and ion exchange capacity with increasing the synthesis period. The samples were used as potential basic catalysts in the transesterification of the waste products of corn oil. The produced sodalite sample after 48 h (SD-48) achieved the best catalytic activity and the best biodiesel yield (95.4%). This yield was obtained after 120 min at 70 °C using 16:1 methanol-to corn oil molar ratio and 4 wt., % SD-48 loading. The achieved yields by SD-24 and SD-72 are 84.7% and 90.5%, respectively. The higher activity of SD-48 (95.4%) than SD-24 (84.7%) related to its high surface area and total basicity. The lower activity of SD-72 (90.5%) than SD-48 (95.4%) related to its very high ion exchange capacity which increases the saponification reactions in the existence of K⁺ and Na⁺ ions at high concentrations. The used SD-48 catalyst shows significant regeneration belongings and reused in five cycles producing valuable biodiesel yields. Technically, the resulted biodiesel from the waste product of corn oil over SD-48 is of acceptable international qualification which prompts the large-scale use of the catalyst.

1. Introduction

The continuous growth of the world’s population, industrialization, and urbanization resulted in an extensive increase in the demand of energy supplies and fossil fuel consumption [1, 2]. Furthermore, the awareness of the contemporary world by the environmental and health dangerous impacts directed the trends of the population towards clean and renewable fuels [3, 4]. Biofuels were evaluated as an alternative for the traditional petroleum-based fuels to match the environmental and health specifications including the low pollution potential and low emission of greenhouse gases [5].

Biodiesel is one of the eco-friendly biofuels that are of very low CO₂, sulfur, NOₓ, and BTEX emissions in addition to its biodegradable properties [2, 6]. Additionally, it is a highly qualified fuel of promising technical properties such as excellent viscosity, lubricity, high flash point, high combustion efficiency, and high octane number [7]. The previous technical properties of biodiesel qualify it to be applied directly into the engines especially as blends with other types of petroleum-based fuels [8–10]. It is fatty acid alkyl esters (FAAEs) which were derived commonly from long-chain triglycerides of different green resources as edible and non-edible plants and vegetable-based oil in addition to the animal fats, algae extracts, and microbial oils [5]. Recently, the
waste products of the cooking oil as corn oil and sunflower oil were recommended as commercial alternatives for fresh edible or nonedible oil [4, 11]. Additionally, it is a highly motivated recycling technique that is of environmental impact in reducing such types of liquid wastes.

The transesterification reaction is the essential technique for the conversion process. It involves a reaction between alcohol and the selected oil in the existence of a suitable catalyst to accelerate the interaction rate [12]. However, the homogenous forms of the catalysts are of higher activity than the heterogeneous catalysts, they are of toxic byproducts, expensive cost, corrosion effect, and difficult separation properties [2, 13]. Therefore, the heterogeneous forms were recommended to avoid the previous environmental and technical drawbacks of the homogenous forms. Additionally, the heterogenous forms are of low production cost, considerable recyclability, and high thermal stability [5, 14]. Still, the essential challenges for commercial use of the heterogeneous forms are the reduction in the fabrication cost, the availability of their precursors, the enhancement of their activities, and the suitable mixing techniques [15].

Alkali (K⁺, Na⁺, Ca⁺², Mg⁺²) bearing heterogeneous catalysts especially those delivered from natural minerals and rocks represent active research points for the researchers as they are low-cost materials of very high natural reserves [2, 4, 16]. Silicate and aluminosilicate minerals represent promising raw materials for the synthesis of such types of active basic catalysts [17, 18]. From the tectosilicate minerals, different species of zeolite (zeolite-P, phillipsite, zeolite-A, Zeolite-Y, mordenite, and zeolite-X) were reported as active heterogeneous catalysts either in their pure phase or after the functionalization of them [15, 16, 19]. They are of nanoporous structures and exhibit excellent surface area, flexible crystalline structures, and high ion exchange properties. Additionally, they are of high mechanical, chemical, and thermal stability to be incorporated in the reaction systems at high temperature [20, 21].

The properties of the synthetic zeolite including its morphology, its porous structure, and its catalytic activity depend mainly on the used precursor and the synthesis conditions [15, 22]. Different species of synthetic zeolite were produced from the natural resources (clay minerals as kaolinite and bentonite) by alkaline hydrothermal transformation reactions using NaOH [23–25]. The resulted zeolitic phases from such clay minerals are dominated mainly by sodium ions as the effective catalytic sites. Additionally, they are of relatively high costs as compared to the other natural precursors [26]. Recent studies demonstrated the suitability of muscovite natural mineral to be used as a precursor in the synthesis of three types of zeolite (phillipsite, sodalite, cancrinite) [23, 26]. The muscovite mineral is a known form of phyllosilicate mica minerals that is of hydrated aluminosilicate structure and enriched in potassium ions that represent the binding layer between its essential units [23, 27].

Unfortunately, the deep investigation for the technical properties of muscovite-based Na⁺⁺/K⁺ synthetic zeolite forms as new basic catalysts has not been covered by satisfactory studies yet. Therefore, this work aims to (1) synthesize a series of Na⁺⁺/K⁺ bearing sodalite of different morphologies from muscovite, (2) investigate the textural and chemical properties of the synthetic forms, (3) follow the catalytic behavior of the synthetic forms as basic catalysts in the transesterification of waste corn oil, and (4) explaining the predicted mechanisms that occurred during the transesterification reactions.

2. Experimental work

2.1. Materials

Muscovite flakes were collected as a natural mineral from feldspar and mica mine (Wadi Mubarak mine), Eastern Desert, Egypt. NaOH pellets (Alfa Aesar, purity: 97%) were used in the hydrothermal production of sodalite. Methanol (99.8%, Sigma Aldrich) and spent commercial corn oil were used in the transesterification tests.

2.2. Synthesis of the sodalite catalyst

Firstly, the muscovite flakes were ground to smaller fractions of particle size from 20 μm to 100 μm using a home blender. The ground muscovite then was calcinated at 950°C as a thermal activation step before the alkaline activation. The activated muscovite (3 g) was mixed with sodium hydroxide solution (6 g) in 100 ml distilled water and the formed mixture (Mu/NaOH) stirred for 180 min at room temperature. After that, the mixture (Mu/NaOH) was transferred into a closed hydrothermal system of Teflon lined with stainless which treated thermally at 150°C for different alteration intervals (24 h, 48 h, and 72 h). Then, the precipitated powders were collected and washed five times for 10 min using distilled water to avoid the effect of the excess in NaOH. Finally, the obtained powder samples were dried at 80°C for 12 h and labeled as SD-24, SD-48, and SD-72.
2.3. Characterization of the sodalite catalysts

The formed phases of zeolite were identified using a PANalytical x-ray diffractometer (Empyrean). The used diffractometer is of Cu-Kα radiation and its operating conditions were considered at 20 mA, 40 kV, scanning speed of 5° min⁻¹, and 2θ angles from 5° to 70°. The change in the sodalite morphology was followed using a Scanning Electron Microscope (Gemini, Zeiss-Ultra 55). Prior to the imaging step, the sodalite powders were coated with a thin gold layer, and the accelerating voltage of the microscope during the imaging step was fixed at 30 kV. The chemical structures of SD-24, SD-48, and SD-72 phases were addressed using two techniques; the first technique is the energy dispersive x-ray (EDX) and the second technique is Fourier Transform Infrared spectrometer (FTIR-8400S). Texturally, the surface area and the pore size distribution of SD-24, SD-48, and SD-72 were evaluated based on their N₂ adsorption/desorption curves which were obtained using the Beckman Coulter surface area analyzer (SA3100 type). The basicity of SD-24, SD-48, and SD-72 was determined according to the reported method by Abukhadra and Sayed [28]. The products (0.5 g) were mixed with dilute HCl solution (20 ml distilled water + 50 ml HCl) for 24 h at a fixed stirring speed (500 rpm) as separated experiments. After that, 25 ml of the three solutions were titrated using an alkaline solution of NaOH (0.1M) in the presence of a chemical indicator (phenolphthalein). The ion exchange capacities of SD-24, SD-48, and SD-72 were determined by the BaCl₂ technique according to Dardir et al [29]. The products (1 g) were mixed homogeneously with aqueous solutions of hydrated barium chloride. Then, the SD-24, SD-48, and SD-72 powders were extracted from the solutions by filtration and dispersed in ammonium acetate solutions (300 ml; 1N) at pH 7 as the releasing environment of the exchangeable Ba⁺² ions. The concentrations of the liberated Ba⁺² ions were measured by ICP-MS (Perkin Elmer) as an indicator for the ion exchange capacities of SD-24, SD-48, and SD-72.

2.4. Transesterification tests

The used system in this study consists of four essential parts; (A) transesterification glass reactor of 250 ml total volume, (B) a reflux system composed of glass condenser to keep the used alcohol in the system, (C) digital magnetic stirrer with magnet bar (3 cm) as the used mixing technique, and (D) hot plate of the digital controller to adjust the temperature of the reaction. The essential variables which were tested during the study are the temperature, the time intervals, the sodalite loading, and the methanol content. The typical procedures which were followed during the accomplishing of the tests involved firstly filtration of the used waste corn oil (40 g) to remove the present solid suspensions. This was followed by heating the filtrate corn oil at 70 °C for about 15 min to avoid the predicted side effects of humidity or the mixed water molecules. After cooling, the oil sample was heated again until attending the selected transesterification temperature. Then, certain quantities of SD-24, SD-48, and SD-72 were mixed with the corn oil for 10 min to ensure the effective dispersion of the sodalite grains.
within the corn oil samples. After that, the alcohol was added according to the selected ratios and left in the reaction for certain time intervals.

By the end of the conducted transesterification experiments, the oil samples were filtrated to separate the sodalite particles. Then, they were poured into glass separating funnels as a principal step to achieve the complete separation of the dense glycerol layer from the generated biodiesel. After isolating the glycerol layer, the generated biodiesel samples were transferred into the oven and heated at 70 °C for about 4 h to ensure that they are free from the unreacted alcohol. The concentration of the generated fatty acid methyl esters was measured using gas-chromatography of Agilent 7890A type after the dilution of them by n-hexane and in the existence of methyl heptadecanoate as an internal standard. The gas-chromatograph system connected with the injector (split/splitless), detector (flame ionization), and DB WAX capillary column (30 m × 0.25 m × 0.25 μm) of inert H2 carrier. Considering the obtained results, the percentages of the achieved biodiesel yields were calculated from equation (1):

\[
\text{Biodiesel yield (\%)} = \left( \frac{\text{Weight of biodiesel} \times \text{\% FAME}}{\text{Weight of oil}} \right) \times 100
\]

3. Result and discussion

3.1. Characterization

3.1.1. Structural properties

The used mica sample is a pure muscovite mineral and this was confirmed by detecting its distinguishing peaks and the related crystallographic planes of monoclinic crystals. The essential peaks were identified at 8.91° (002), 17.82° (004), 26.84° (006), 36° (008), and 45.47° (0010) (Ref. Code. 01-084-1303) (figure 1(A)). The inspection of the crystalline structure demonstrated the formation of the muscovite with a crystallite size of 54 nm and a microstrain of 0.239%. After the thermal activation, the pattern of the heated muscovite sample shows the same peaks of raw muscovite but with recognizable shifting to the lower positions and noticeable declination in their intensities (figure 1(B)). The positions of the muscovite crystal were reported at 8.75°, 17.56°, 26.49°, 35.59°, and 44.92° (figure 1(B)). The heating process affected strongly the crystallite size as well as the perfection of the crystal. The crystallite size and the microstrain increased to 69 nm and 0.264%, respectively reflecting the role of temperature in agglomerating the muscovite grains and the partial destruction of the muscovite lattice structure.

Figure 2. SEM images of raw muscovite (A), sodalite grains after 24 h (SD-24) (B), sodalite grains after 48 h (SD-48) (C), and sodalite grains after 72 h (SD-72) (D).
The patterns of SD-24, SD-48, and SD-72 reflected clearly the complete alteration of muscovite into highly crystalline sodalite (Ref. Code. 04-009-5259). The sodalite peaks of SD-24 observed at 14.06°, 24.49°, 31.78°, 34.93°, 37.87°, and 43.13° in addition to other minor peaks (figure 1(C)). For SD-48, the essential peaks signified to 14.08°, 24.52°, 31.82°, 34.95°, and 43.16° (figure 1(D)). The sodalite peaks of SD-72 observed at 14°, 24.41°, 31.69°, 34.81°, 37.92°, and 43.03° in addition to other minor peaks (figure 1(E)). These peaks corresponding to (110), (221), (310), (222), (321), and (330) lattice planes of cubic sodalite (Ref. Code. 04-009-5259). Such changes in the positions of the sodalite peaks of SD-24, SD-48, and SD-72 might be of considerable indications about internal changes either in the elemental composition of the structural units or their dimensions. This appeared also in their crystallite sizes, the calculated values of SD-24, SD-48, and SD-72 are 52.4 nm, 49.6 nm, and 47.2 nm, respectively. This will be of observable influence on the catalytic behaviors of the muscovite-based sodalite phases during their incorporation in the transesterification reactions.

3.1.2. Morphological properties
The SEM images of the sodalite particles revealed morphological reformation of the muscovite raw material into new synthetic material of different morphology. The raw muscovite is of high crystalline properties with the characteristic flakey form (figure 2(A)). After the alkaline treatment, the muscovite flakes were transformed into new crystals of different morphologies which are related to the produced sodalite after different time intervals (figures 2(B)–(D)). After 24 h as alteration time (SD-24), the sodalite grains appeared as well-developed hexagonal disks of well crystalline properties (figure 2(B)). After an alteration time of 48 h (SD-48), the sodalite grains were detected in the typical octahedron form that characterizes the crystals of the cubic system reflecting the influence of the time in directing the morphology (figure 2(C)). This was detected also for the sodalite grains after 72 h (SD-72), the sodalite grains appeared as prismatic crystals in twinning forms and intersect with each other forming a flower-like shape (figure 2(D)). Such morphological form is of positive influence in inducing the surface area as well as the exposure of the active catalytic sites. Moreover, the detected clear changes in the morphologies of sodalite might be related to predicted changes in the chemical internal structures and the ordering of the ions in the crystal lattice of sodalite.

3.1.3. Chemical properties
Firstly, the EDX spectrum of the raw muscovite reflected the presence of O, Si, Al, K, Fe, Na, and Mg at percentages of 50.45%, 22.53%, 16.8%, 7.0%, 2.6%, 0.39%, and 0.23%, respectively (figure 3(A)). The transformation of muscovite into sodalite resulted in significant changes in the percentages of the essential elements. For SD-24, the present elements are O (52.8%), Si (19.3%), Al (13.5%), Na (8.7%), K (5.34%), and Fe

Figure 3. EDX spectra of raw muscovite (A), sodalite grains after 24 h (SD-24) (B), sodalite grains after 48 h (SD-48) (C), and sodalite grains after 72 h (SD-72) (D).
The effect of such chemical changes on the essential functional groups was followed based on the FT-IR spectra of muscovite, SD-24, SD-48, and SD-72 (figure 4). The essential groups of muscovite as hydrated aluminosilicate mineral were identified clearly at 3620 cm\(^{-1}\) (OH), 1650 cm\(^{-1}\) (adsorbed water), 1022 cm\(^{-1}\) (Si–O–stretching), 923 cm\(^{-1}\) (Si–O–Si), 878 cm\(^{-1}\) (Al–O–H), 783 cm\(^{-1}\) (Al–O–Al), 690 cm\(^{-1}\) (Si–O–Al), and 533 cm\(^{-1}\) as well as 472 cm\(^{-1}\) (Si–O–Si) (figure 4(A)). The FT-IR spectra of synthetic sodalite samples (SD-24, SD-48, and SD-72) displayed the same bands of muscovite but at deviated positions (figures 4(B)–(D)). This reflects the influence of the alkaline transformation reactions on the structural groups of muscovite and the incorporation of new ions. There is an observable intensification in the OH-related bands which signifies the role of the alkaline conditions in causing etching for the existed siloxane groups. This results in more exposure for such groups and in turn induces the surface basicity of the products [24].

3.1.4. Textural and physicochemical properties

Texturally, the surface area showed a significant increase by expanding the synthesis time of sodalite from 24 h to 72 h (table 1). The measured surface area of muscovite, SD-24, SD-48, and SD-72 are 6.2 m\(^2\) g\(^{-1}\), 73.2 m\(^2\) g\(^{-1}\), 94.6 m\(^2\) g\(^{-1}\), and 105 m\(^2\) g\(^{-1}\), respectively. This reflects the enhancement in the crystallinity and porous structure of sodalite with the synthesis time in addition to the previously reported changes in the morphologies especially for the synthetic sample after 72 h (SD-72). This was reported also for the porosity properties, the pore volume increased from 0.173 cm\(^3\) g\(^{-1}\) for muscovite to 0.182 cm\(^3\) g\(^{-1}\), 0.201 cm\(^3\) g\(^{-1}\), and 0.220 cm\(^3\) g\(^{-1}\) for SD-24, SD-48, and SD-72, respectively (table 1). The measured average pore size diameters for raw muscovite, SD-24, SD-48, and SD-72 are 18.3 nm, 11.6 nm, 6.2 nm, and 8.3 nm, respectively (table 1). The reported higher pore size
diameter for SD-72 than SD-48 might be related to the role of the morphological properties of SD-72 in providing secondary micropores [26].

The previous changes in the crystalline, morphological, chemical and textural properties resulted in significant changes in the physicochemical properties especially the total basicity and the ion exchange capacity. The determined ion exchange capacities of muscovite, SD-24, SD-48, and SD-72 are 3.12 meq/100 g, 36.7 meq/100 g, 50.6 meq/100 g, and 71.3 meq/100 g, respectively (table 1). Additionally, the total basicity emphasized an obvious increase with increasing the synthesis time. The measured total basicity of SD-24, SD-48, and SD-72 is 5.33 mmol OH/g, 6.41 mmol OH/g, and 4.34 mmol OH/g, respectively which is of significant agreement with recognized chemical properties (table 1). Moreover, these values qualify the synthetic sodalite products to be applied as basic catalysts in the transesterification of corn oil into biodiesel.

3.2. Transesterification results

3.2.1. Effect of the essential variables

3.2.1.1. Effect of time

The transesterification interval is a critical factor either in controlling the transesterification rates or transesterification efficiency. The transesterification intervals were examined from 15 min until 240 min (figure 5). The main experimental variables were selected based on primarily studies to be at fixed values of 2 wt.%, 12:1, 60 °C, and 800 rpm for the used sodalite loadings, the incorporated methanol-to-corn oil molar ratio, the adjusted temperature, and the stirring speed, respectively.

Generally, the catalytic activities of SD-24, SD-48, and SD-72 showed noticeable changes with time which was reflected in the percentages of the generated biodiesel as well as the achieved transesterification rates (figure 5). Conducting the reactions for short intervals resulted in low yields and limited variation in the corn oil transesterification rates. This was reported from 15 min to 60 min for SD-24 and SD-48, and 15 min to about 45 min for SD-72 (figure 5). After these intervals, the catalytic performances of them induced greatly, and the corn oil transesterification rates accelerated strongly producing significant biodiesel yields. The accomplishment of the experiments for short intervals will not provide a sufficient chance for the effective interaction between the reactants, the homogeneity between them, and the miscibility between the liquids reactants which reduce the

![Figure 5. The influence of the time intervals in the transesterification of corn oil over the synthetic sodalite samples (SD-24, SD-48, and SD-72).](image)

| Sample     | Specific surface area (m² g⁻¹) | Total volume (mL g⁻¹) | Average pore diameter (nm) | Cation exchange capacity (meq/100 g) | Basicity (mmol OH/g) |
|------------|--------------------------------|-----------------------|----------------------------|-------------------------------------|----------------------|
| Muscovite  | 6.2                            | 0.173                 | 18.3                       | 3.12                                | 3.86                 |
| SD-24      | 73.2                           | 0.182                 | 11.6                       | 36.7                                | 5.33                 |
| SD-48      | 88.6                           | 0.201                 | 6.2                        | 50.6                                | 6.41                 |
| SD-72      | 105                            | 0.220                 | 8.3                        | 71.3                                | 4.34                 |
catalytic effect of the catalysts and in turn the reaction efficiency [30]. The miscibility, homogeneity, and interaction chances can be prompted successfully by expanding the mixing time intervals until attending the best time of the best biodiesel yields [30]. The best intervals for using SD-24, SD-48, and SD-72 are 135 min, 120 min, and 90 min, respectively which resulted in biodiesel yields of 57.3%, 71.3%, and 66.2% in order (figure 5).

Beyond, the previously presented best intervals, the reactivity of SD-24, SD-48, and SD-72 catalysts as a function of the determined biodiesel yields declined to lower values (figure 5). The transesterification as a reversible reaction depends mainly on the selected interval as the uncontrolled increase in the reaction time causes hydrolysis for the created esters which convert them again to their original free fatty acids [5, 31]. The reported variation in the best time intervals for the sodalite varieties (SD-24, SD-48, and SD-72) might be credited to their differences in particle size, reactivity, and other surficial properties. Such differences affected strongly their mixing properties and their catalytic activities. However the SD-72 sample is of higher basicity and surface area than the SD-48 sample, it achieved lower yields than it at all the studied intervals. This can be credited to the high ion exchange capacity of SD-72 as it increases the released free K\textsuperscript{+} and Na\textsuperscript{+} ions into the corn oil/methanol mixture causing a saponification effect which is of negative influence on the reaction rate [28].

3.2.1.2. Effect of temperature
Adjusting the system at its best temperature value is critical to accelerating the transesterification of corn oil over the sodalite varieties (SD-24, SD-48, and SD-72) (figure 6). The temperature effect was followed from 30 °C to 100 °C considering the other affected variables at 2 wt., %, 12:1, and 800 rpm for sodalite loadings, methanol-to-corn oil molar ratio, and the stirring speed, respectively. The time intervals were adjusted at 135 min, 120 min, and 90 min for SD-24, SD-48, and SD-72, respectively.

The sodalite catalytic performances and the associated biodiesel yields induced obviously with the ascendant changes in the temperature until certain values (figure 6). Normally, as transesterification is an endothermic reaction, it can be accelerated and induced by adjusting the temperature of the system at high-temperature conditions [5]. Additionally, the high-temperature conditions decline efficiently the viscosity of corn oil which enhances the miscibility with the alcohol molecules as well as the mixing properties between the solid and liquid reactants [4]. The preferred temperature value for the best transesterification of corn oil over SD-24 is 80 °C (64.7%) while the preferred value for SD-48 and SD-72 is 70 °C with yields of 80.4% and 72.3%, respectively (figure 6). Adjusting the reactions at a temperature above the previously mentioned values (80 °C (SD-24) and 70 °C(SD-48 and SD-72)) is of undesirable effect and the appreciated yields reduced observably (figure 6). This demonstrated the uncontrolled escape and evaporation of methanol from the systems at such conditions which are of disturbing effect on the balance between the reactants and cause a reduction in the formed esters [32, 33].

![Figure 6. The influence of the reaction temperature in the transesterification of corn oil over the synthetic sodalite samples (SD-24, SD-48, and SD-72).](image-url)
3.2.1.3. Effect of methanol-to-oil molar ratio

The alcohol molecules are essential components during the transesterification reaction as the formation of the biodiesel involved essentially interaction between three moles of it and one mole of oil [34]. Therefore, adjusting the ratio between the corn oil and the used methanol is of principal role in lowering the immiscibility, endorsing the mass transfer rate, and balancing the reaction which induced the rate of the reaction in the forward side [2].

The predicted influence of the used methanol ratios was followed considering its molar ratio to corn oil from 10 (methanol):1 (corn oil) to 20 (methanol): 1 (oil) (figure 7). The other affected variables were considered at 2 wt., %, and 800 rpm for sodalite loadings and stirring speed, respectively. The time intervals were adjusted at 135 min, 120 min, and 90 min for SD-24, SD-48, and SD-72, respectively. Also, the temperature values were adjusted at 80 °C for SD-24 and at 70 °C for SD-48 and SD-72.

The catalytic performances of the sodalite varieties were persuaded clearly with the ascended changes in the alcohol molar ratio from 10 (Mth):1 (C.O) until 16 (Mth):1 (C.O) for the three sodalite varieties (figure 7). The biodiesel yields at this ratio (16 (Mth):1 (C.O)) are 72.3%, 89.4%, and 81.5% for SD-24, SD-48, and SD-72, respectively (figure 7). Studying the methanol content at ratios higher than 16 (Mth):1 (C.O) revealed undesirable effects and declination in the extracted biodiesel yields from corn oil (figure 7). Such adverse behavior is related to several reasons including (1) deactivation of the sodalite active sites by the free methanol
molecules, (2) the over alcohol content is of undesirable impact on the reaction balance, (3) the free alcohol molecules are of dissolving affinity for the resulted glycerol molecules which direct the process to the reversible side, and (4) the predicted inversion for the alcohol polar groups resulted in emulsifier centers which hinder the transesterification rate [1, 5, 15].

3.2.1.4. Effect of sodalite loading

The possible enhancement of the corn oil transesterification by using different sodalite loading was studied from 1 wt., % until 5 wt., % (figure 8). The stirring speed and the methanol-to-corn oil molar ratio were fixed at 800 rpm and 16:1, respectively. The time intervals were adjusted at 135 min, 120 min, and 90 min for SD-24, SD-48, and SD-72, respectively. The temperature values were adjusted at 80 °C for SD-24 and at 70 °C for SD-48 and SD-72.

The activity of sodalite in inducing the corn oil transesterification reaction enhanced strongly with the ascending changes in the used sodalite loadings from 1 wt., % until 4 wt., % (figure 8). The high sodalite loadings are associated with an increase in the exposed active sites as well as the surface area which provides more chances for the interaction area with the other components [8, 34]. The biodiesel yields which were obtained using this sodalite loading (4 wt., %) are 84.7%, 95.4%, and 90.5% for SD-24, SD-48, and SD-72, respectively (figure 8). Applying the sodalite varieties in the system at higher loading than 4 wt., % appears to be of negligible effect or of slight negative impact (figure 8). The saturation of the system by the fine particles of sodalite over the limit can increase the viscosity which in turn reduces the mixing as well as the homogeneity between the three reacting components [2, 5].

3.2.2. Mechanism

Based on the previously reported results, the synthesis of sodalite from muscovite is a promising potential basic catalyst of two active sites (Na⁺ and K⁺) and can be applied in the transesterification of corn oil with significant yields. Additionally, the synthesis time of sodalite is of an effective role in controlling the morphology, basicity, reactivity, surface area, and ion exchange properties of the product which are the essential parameters that affect directly its catalytic performance. Therefore, increasing the synthesis time from 24 h (SD-24) to 48 h (SD-48) resulted in a strong increment in the obtained biodiesel yield. However, the sodalite sample that was synthesized after 72 h (SD-72) is the best sample regarding the textural and basicity properties; it achieved lower catalytic performance than the prepared sample after 48 h (SD-48). This was followed chemically by detecting the K⁺ and Na⁺ content in the resulted biodiesel. The detection of Na⁺ and K⁺ at high concentrations in the biodiesel samples after using SD-72 reflected the role of its very high ion exchange capacity in releasing such ions in insufficient concentrations which are of saponification effect and affect negatively the reaction.
Generally, the mechanism can be described based on the nature of the used catalyst and its essential active catalytic sites (figure 9). The synthetic sodalite from muscovite is a novel form enriched in both the sodium and potassium ions as strong basic catalytic centers (figure 9). The potassium ions in the structure of sodalite play the main role in the transesterification of corn oil. By the initiation of the reaction, the methanol molecules adsorbed by the active sites of the sodalite catalysts (SD-24, SD-48, and SD-72), and during this process, the hydrogen protons of methanol abstracted strongly by the structural potassium ions (figure 9). The normal ion exchange between the existing potassium ions and the existed methanol molecules resulted in the generation of CH$_3$O$^-$ (alkoxide anion) (figure 9). At the same time, portions of the generated fatty acids adsorbed effectively by the siloxane groups of sodalite (OHearing groups) forming new species of physical bonds with the functional carbonyl groups. The generated alkoxide anion (CH$_3$O$^-$) then attacked the functional carbonyl groups after the protonation of them which produce a series of esters in the system [5] (figure 9). The acidity properties of the alcohol molecules that adsorbed by sodalite cause the formation of methoxide moieties cover on its surface (figure 9).

The other essential component in the structure of sodalite is the sodium ions that are vital radical that controls the catalytic activity of it (figure 9). The Na$^+$ based moieties on the surface of the sodalite products accelerate the formation of methoxide moieties. This takes place after the stabilization of both the basic sites and the methanol-related protons by the present acidic sites. The acidic sites in the sodalite structure are the basal oxygen ions of silica tetrahedron and alumina octahedron (figure 9).

### 3.2.3. Regeneration properties

The regeneration capacity of sodalite to be recycled several runs in the production of biodiesel from corn oil is a vital parameter for the commercial and large-scale application of it as a catalyst. The regeneration procedures involved the washing of the sodalite grains with methanol and distilled water for 10 min. Then, the sodalite grains were dried at 80 °C for 6 h and reused again in another transesterification test. The regeneration study was conducted for the SD-48 sample as it shows the best catalytic activity (figure S1 available online at stacks.iop.org/MRX/8/065502/mmedia). The conditions were adjusted at previously reported best conditions of 4 wt., %, 120 min, 70 °C, 16:1, and 800 rpm for the SD-48 loading, the reaction intervals, the temperature, the methanol-to-corn oil molar ratio, and the stirring speed, respectively.

The results reflected promising regeneration properties and the sodalite catalyst achieved excellent biodiesel yields in five recyclability cycles especially with using methanol as the regeneration reagent (figure S1). The reported preference for methanol as a regeneration reagent for sodalite is related to its strong dissolving affinity for the organic molecules that might be adsorbed during the experiments (figure S1). There is a linear declination in the recognized yield with the regular repeating of the regeneration cycles. This is related to the role of the adsorbed oil and/or glycerol molecules in the deactivation of the sodalite surface by hindering the interaction chances between its basic sites and the other reactants [35]. For distilled water, the recyclability results validated the possible obtained of biodiesel yields more than 92% for two cycles, more than 90% for three cycles, more than 85% for four cycles, and more than 82% for the five cycles (figure S1). For methanol, the obtained yields are higher than 93% for three cycles and higher than 90% for the five cycles (figure S1).

### 3.2.4. Technical properties of the formed biodiesel

The technical specifications of the generated biodiesel using SD-48 were evaluated considering the recommended limitations by ASTM D-6751 and EN 14214 international standards (table 2). Generally, the reported properties match widely the technical limitations of both ASTM D-6751 and EN 14214. The cetane index of the sample is higher than 45 and this qualifies the product to be used as safe fuel in the traditional

| Contents            | Unit   | ASTM D-6751 | EN 14214 | Biodiesel sample |
|---------------------|--------|-------------|----------|-----------------|
| Viscosity           | mm² s⁻¹| 1.9–6       | 3.5–5    | 3.6             |
| Moisture content    | Wt. (%)| <0.05       | <0.05    | 0.041           |
| Flashpoint          | °C     | >120        | >120     | 133.5           |
| Cloud point         | °C     | -3 to 15    | —        | 8.7             |
| Pour point          | pp     | -5 to 10    | —        | 6.2             |
| Cetane number       |        | 47–65       | 51 to 120| 61.4            |
| Density             | g cm⁻³ | 0.82–0.9    | 0.86–0.9 | 0.85            |
engines with little emissions [4, 16]. The viscosity of the sample also is of sufficient value to be used directly in the lubrication, fuel atomization, and fuel injectors industries. Moreover, the measured flashpoint clarifies the safe properties of the product for further handling, sorting, and transportation processes [16].

3.2.5. Comparison study
The activity of SD-48 was compared with SD-24 and SD-72 and other catalysts as a function of the achieved yields (table S1). It was achieved higher results than the investigated homogenous and heterogeneous catalysts as MgO, NaOH, KOH, CaO/SiO2, and CaO/γ-Al2O3. This gives the muscovite-based sodalite commercial value as it is of low cost, available precursor, and environmental properties.

4. Conclusion
Three species of K+ and Na+ bearing sodalites samples were prepared from muscovite after 24 h (SD-24), 48 (SD-48), and 72 h (SD-72)) as potential catalysts in the transesterification of waste corn oil. The three species are of different, morphologies, chemical composition, surface area, total basicity, and ion exchange capacity. However, the SD-72 is of the best basicity and surface area it achieved lower activity than SD-48 as it is also of high replacement capacity of Na+ and K+ which are of strong saponification effect. The obtained yield by SD-48 is 95.4% and was determined after 120 min at 70 °C using 16:1 methanol-to corn oil molar ratio, 4 wt., % loadings. The SD-48 as a catalyst is of high recyclability for five cycles which appear in the determined valuable biodiesel yields. The resulted biodiesel over SD-48 is of acceptable specifications according to international standards.

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Data availability statement
The data that support the findings of this study are available upon reasonable request from the authors.

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