# Effect of calcination temperature and reactant impurities on the performance of a heterogeneous catalyst based on magnetic iron and alkali metal in a biodiesel production process

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*Abstract*— The activity and efficiency of heterogeneous catalysts used for biofuel production depend on their preparation conditions and the purity of the reagents. In addition, their large-scale use depends on their ability to be reused over several cycles. Our work focuses on the preparation and use of a more reusable heterogeneous catalyst based on magnetic iron impregnated with alkali metal to produce biodiesel. This catalyst was prepared by wet impregnation followed by calcination. The effect of the calcination temperature of the material, the calcination time and the iron hydroxide/alkali metal ratio were evaluated. In addition, the content of FFA and water as impurities in the reagents was analysed. The synthesised material was characterised by ATG, IR-FT and the Hammett indicator method before being used for transesterification. The ester content of the biodiesels produced was quantified by GC. The results of the analysis show that this catalyst is efficient with an ester content of the biodiesel of over 90%. The preparation conditions were: calcination temperature at 400°C, calcination time at 2h, and impregnation ratio at 1/1. The catalyst also remained effective in the presence of an oil with a FFA content of more than 2% and an alcohol water content of 3%. The catalyst is reusable over at least two cycles without post-treatment with a biodiesel ethyl ester content of over 90%.

Keywords-Biodiesel, heterogeneous catalyst, ferrous iron, alkali metals, reusability.

#### I. INTRODUCTION

The transesterification reaction of vegetable oils makes it possible to produce green fuels locally in a West African context known for its recurring energy crises. This energy-intensive reaction is generally carried out using catalysts, which reduce the time needed to obtain biodiesel and thus cut production costs. The activity and efficiency of heterogeneous catalysts, known for their low carbon borrowing and increasingly used for the production of this biofuel, depend on the conditions under which they are prepared and the purity of the reagents [1]. In addition, their large-scale use depends on their ability to be reused over several cycles [2]. Magnetic-based heterogeneous catalysts are more reusable because of their higher recovery capacity [2]. To improve their reusability, magnetic-based materials are being developed for use as catalyst supports for heterogeneous catalysts. However, these materials show low activity when used without combinations with active precursors. As a result, materials that have demonstrated their effectiveness in transesterification, such as alkali metals, are being used to boost their activity [3]. In addition, according to [4], the basicity and transesterification activity of catalysts impregnated with alkali metals increases as the size of the active precursor alkali metal ion decreases. However, other studies have shown that this basicity and activity depend more on the active phases present on the surface of the catalyst, which appear during the heat treatment of the material [3]. This highlights the difficulty in choosing the best active precursor. This research focuses on the preparation of a heterogeneous catalyst based on magnetic iron impregnated with alkali metal for biodiesel production. Our work deals specifically with the choice of alkali metal active precursor by analysing the physicochemical parameters for preparing the catalyst, as well as content of free fatty acids (FFA) and water as impurities in the reagents on the performance of the catalyst. Finally, the reusability of the catalyst over several biodiesel production cycles was assessed.

## II. MATÉRIEL AND METHODES

## A. Matériel

The material used in our work consisted of FeSO<sub>4</sub>•7H<sub>2</sub>O from SIGMA-ALDRICH (purity  $\geq$  98%), Fe(NO<sub>3</sub>)<sub>3</sub>•9H<sub>2</sub>O and ammonia (purity = 28%) from VWR International S.A.S., used for the synthesis of a magnetic oxide precursor. KOH (M = 56.11 g/mol), NaOH (M = 40.00 g/mol), both from Charlab S.L., and LiOH from SIGMA-ALDRICH Co (purity  $\geq$  98%), were used as the active precursor for the preparation of the catalyst. Bromothymol blue (H\_ = 7.2), phenolphthalein (H\_ = 8.2), 2,4 - dinitroaniline (H\_ = 15) and nitroaniline (H\_ = 18.4), all purchased from SIGMA-ALDRICH, absolute methanol (purity = 100%), from VWR International S.A.S, and benzoic acid (purity  $\geq$  99.98%), were used to determine the basicity of the catalysts. Refined sunflower oil (brand name: BONITA) and anhydrous ethanol (brand name: Chem-Lab NV) were used as reaction reagents. A standard sample of ethyl heptadecanoate (purity  $\geq$  97%) from Santa Cruz Biotechnology and n-Hexane (purity  $\geq$  99%), all from VWR International S.A.S, were used for the gas chromatographic (GC) analysis of the biodiesel samples.

## B. METHODES

1) Catalyst synthesis :...The magnetic iron precursor [Fe(II), Fe(III)] was synthesised by coprecipitating the Fe<sup>2+</sup>/Fe<sup>3+</sup> ions contained in a solution prepared at equimolar concentration of FeSO<sub>4</sub>•7H<sub>2</sub>O and Fe(NO<sub>3</sub>)<sub>3</sub>•9H<sub>2</sub>O with a basic solution of ammonia (28 %). The precipitate obtained was filtered and washed abundantly with deionised water and the substrate obtained was dried for approximately 24 h at 105°C in an oven, then ground in a porcelain mortar to obtain a particle size fraction of less than 0.315 mm. This magnetically active sample was washed and dried and ground again, graded Fe(II)@Fe(III) and packed in a hermetically sealed vial and stored in a desiccator.

2) *Catalyst characterisation* :..The thermal behaviour of the various materials was studied using thermogravimetric analysis (TGA). The basic properties of the various catalysts were assessed using the Hammett-benzene carboxylic acid indicator titration method. In addition, the surface chemical functions of the different materials were analysed using a Bruker ALPHA Fourier transform infrared spectrometer in TAR (Total Attenuated Reflection) mode between 4000 and 400 cm<sup>-1</sup> at a resolution of 0.1.

*3) Transesterification tests and biodiesel characterisation* :...The biodiesel synthesis was carried out using the reaction conditions optimised by [5] and readapted following preliminary tests carried out. At the end of the reaction, the catalyst was separated from the products by centrifugation and the excess ethanol in the sample was evaporated using a BUCHI Switzerland R-300 rotary evaporator. The reaction product was left to stand in a separating funnel until the biodiesel phase and glycerol phase were separated. The upper biodiesel phase containing the ethyl esters is taken for analysis by gas chromatography (GC). The standard NF EN 14103 method was used to quantify the ester content of biodiesel samples.

To test its ability to be reused over several transesterification reaction cycles, the catalyst is isolated by centrifuging the products at the end of the reaction time, then reintroduced directly (without post-treatment) into the reactor for the next cycle. The reaction conditions are maintained unchanged.

## III. RESULTS

## A. Catalyst characterisation

The thermograms of our various materials recorded, and presented in Fig. 1, show that our materials undergo thermochemical phenomena essentially in three temperature ranges. The first phenomenon, marked by the highest mass losses (%TA), of around 13.5%, 5% and 7.1% respectively for K/Fe(II)@Fe(III), Na/Fe(II)@Fe(III) and Li/Fe(II)@Fe(III), takes place around 105°C and could probably be due to a dehydration phase of the free water mixture contained in our materials. Next, the successive mass loss phenomena can be observed between approximately 180 and 650°C and correspond to the dehydroxylation of iron and alkali metal hydroxides. Finally, the last phenomenon, in which mass losses occur between approximately 650°C and 850°C, is thought to be linked to the formation of alkali metal ferrites and/or gasification of oxides from the network of oxides formed previously. Our materials were therefore calcined in the range 200°C to 800°C in order to assess the influence of calcination temperature on their catalytic performance.



and Li/Fe(II)@Fe(III)



Fig. 2: FTIR spectra of K/Fe(II)@Fe(III), Na/Fe(II)@Fe(III) and Li/Fe(II)@Fe(III) calcined at 200°C, 600°C and 800°C for 2 h.

The base strength, which provides information on the basicity of the active phases formed by K/Fe(II)@Fe(III), Na/Fe(II)@Fe(III) and Li/Fe(II)@Fe(III) calcined at 200°C, 600°C and 800°C, was measured and recorded in Table 1. Analysis of the influence of the calcination temperature of the different catalysts on their respective basic strengths shows that overall K/Fe(II)@Fe(III) has a strong basic strength at 15.0 < H\_< 18.4 which remains constant whatever the calcination temperature, suggesting the presence of stronger basic sites generated by the oxide ions (Lewis base) on the surface of this material whatever the calcination temperature. Furthermore, although strong at 15.0 < H\_< 18.4 from 200°C to 600°C, the basic strength of Na/Fe(II)@Fe(III) and Li/Fe(II)@Fe(III) decreases to 7.2 < H\_< 9.8 and H\_< 7.2 respectively when the calcination temperature rises to 800°C. This drop in basic strength at 800°C can be attributed to the presence of moderate or weak basic sites on the surface of the material, which could be due to a molar rearrangement of the initial active phases under the effect of a higher calcination temperature. These results are consistent with those observed on the thermograms, where several phases of thermal decomposition of the different temperature ranges.

<b>Table 1:</b> Basic K/Fe(II)@Fe(III), and		200°C	600°C	800°C	strengths of Na/Fe(II)@Fe(III) Li/Fe(II)@Fe(III)
	K/Fe(II)@Fe(III)	$15 < H_{-} < 18,4$	$15 < H_{<} < 18,4$	$15 < H_{<} 18,4$	
calcined at 200°C, for 2 h	Na/Fe(II)@Fe(III)	$15 < H_{<} < 18,4$	$15 < H_{<} 18,4$	H_<7,2	600°C and 800°C
	Li/Fe(II)@Fe(III)	$15 < H_{-} < 18,4$	$15 < H_{-} < 18,4$	$9,8 < H_{-} < 15$	

In order to evaluate the influence of calcination temperature on the surface functions of our materials, Li/Fe(II)@Fe(III), which experienced a decrease in its basic strength at 800°C, was calcined at different temperatures and its surface functions were analysed by infrared spectrometry (FTIR), with the spectra presented in Figure 2. In the absorption spectrum of Li/Fe(II)@Fe(III) uncalcined and those calcined at 200°C and 600°C, we observed a broad band at about 1483 cm<sup>-1</sup> which could be due to Li—O—H bonds while those at about 1193 cm<sup>-1</sup> and 883 cm<sup>-1</sup> could be related to Fe—O—H and Li—O bonds respectively. Furthermore, compared to the spectrum of non-calcined Li/Fe(II)@Fe(III), we noted on that calcined at 200°C and 600°C, the appearance of a new adsorption band at about 653 cm<sup>-1</sup> which could be attributable to a stretching vibration of the Metal—Oxygen—Metal bond characteristic of lithium ferrite (Fe—O—Li). When the calcination temperature of the material was raised to 800°C, we noted the disappearance of all the vibration bands involving lithium. This could be explained by the vaporisation of the alkali metal at high temperature, as explained in the work of [6]. These results therefore support our analyses of the ATG and basicity data discussed previously and show the influence of calcination temperature on the formation of the active phases of our materials.

## B. Influence of preparation conditions

The results of the transesterification tests carried out with our different catalysts show that K/Fe(II)@Fe(III) has a better catalytic performance compared with Na/Fe(II)@Fe(III) and Li/Fe(II)@Fe(III) (Fig. 3A). The best conversion rates were obtained at 200°C calcination temperature with a conversion rate of 94.86 %. This performance remained virtually stable up to 400°C with a conversion rate of 94.69 %. This high activity at 200°C and 400°C could be justified by a greater number of active phases of high basicity at these temperatures. In addition, a drop-in activity was observed from 600°C onwards, with a conversion rate of around 84.08 %. A further increase in activity was observed at 800°C. This drop in activity followed by a further increase could be explained by a transient phase from homogeneous active phases (K<sub>2</sub>O) to heterogeneous active phases (alkali metal ferrites) or by a momentary molecular reorganisation of the active phases at 600% with fewer basic active phases leading to other more basic active phases [3]. Na/Fe(II)@Fe(III) and Li/Fe(II)@Fe(III), although showing good activity at 200°C and 400°C, have poor performance, with biodiesel ethyl ester contents below the 90 % required to be used alone in a diesel engine as suggested by standard EN 14 103. In addition, for the final choice of the best calcination temperature, a homogeneity test showing the homogeneous contribution of the active phases likely to solubilise and reduce the reusability of the catalyst was carried out and the results presented in Fig. 3B. These show a lower homogeneous contribution from the active phases of the catalyst at 400°C, which can be justified by the presence of a greater number of heterogeneous active phases the surface of the catalyst at this temperature. These results are consistent with those of the FTIR spectra, which show an increase in heterogeneous active sites (alkali metal ferrite) when the calcination temperature is increased from 200°C to 200°C. Therefore, with a view to increasing its reusability in future rection cycles, the temperature of 400°C was chosen as the optimum for the synthesis of our materials.



Fig. 3: Ester content of biodiesel obtained with K/Fe(II)@Fe(III), Na/Fe(II)@Fe(III) and Li/Fe(II)@Fe(III) calcined at different temperatures for 2 h. Reaction conditions: temperature: 70°C, reaction time: 1 h, amount of catalyst: 10%, stirring speed: 300 rpm, oil/ethanol ratio: 1/9.

## C. Influence of open-air storage and reagent impurities and catalyst reusability

The storage conditions affecting the catalytic performance of K/Fe(II)@Fe(III) were analysed by exposing it to ambient air for a period ranging from 3 h to 48 h. The results show a relatively small drop-in activity after 3 h exposure (Fig. 4A). The greatest loss of activity was observed after 6 h of exposure. This could be due to the absorption of free water, which is known to deactivate the catalytic activity of heterogeneous transesterification catalysts. This water reacts with the Lewis oxides ( $O^2$ ), the basic catalytic sites, reducing their number and therefore the activity of the catalyst.

The effect of the free fatty acid (FFA) content, a limiting factor in the efficiency of basic catalysts, was also analysed. The results of the tests carried out show that K/Fe(II)@Fe(III) remains effective in the presence of high levels of FFA (Fig. 4B). In fact, the ethyl ester content produced with this catalyst remains above 90% when the vegetable oil used contains a FFA acid content of 2 % or less (peanut oil, sunflower oil). A decrease in this activity is observed when the vegetable oil used has a FFA content of 13.3 % (balanite oil). The ester content of the biodiesel obtained under these conditions then falls to 82.03%. The greatest drop-in catalyst activity is observed when the FFA content rises from 13.3 % to 37.7 % with an ester content of 7.61 % in the biodiesel. This drop-in activity could be explained by the saponification of these FFAs competing with transesterification. However, the performance of this catalyst in the presence of FFA is much better than that of several other catalysts, including that of Tcheussa and colleagues [6].

In addition, the effect of alcohol purity on the performance of the catalyst was evaluated by injecting different quantities of distilled water in a water/alcohol percentage ratio into the reaction medium. The results

of this test (Fig. 4C) show that the activity of the catalyst remains good and virtually constant up to a water content of 3 %. This is interesting from an economic point of view, given the high cost of anhydrous alcohol on the market. Above this 3% water content, the performance of the catalyst drops significantly, with the ester content of the biodiesel falling to 3 %. This is due to hydrolysis of the triglyceride fatty acids followed by a competitive saponification reaction. The literature shows that a water content of less than 2.5 % is acceptable for a basic catalyst [7] showing a competitive advantage for our material.

The ease of separation and recycling of the heterogeneous catalyst is an important economic and environmental advantage over its homogeneous counterpart. The reusability of the K/Fe(II)@Fe(III) catalyst, which showed better activity, was tested over several reuse cycles and is shown in Figure 4D. The results obtained show good stability of the catalyst's active sites over the first four cycles of reuse, with a slight drop in activity from one cycle to the next, from 94.86% to 82.30%. The first major loss of activity from one cycle to the next was observed between the 4th and 5th cycles, with a drop in the conversion rate of around 15%. This drop in activity could be explained by several phenomena, such as more pronounced leaching of the active phases or the absorption of organic compounds from the reaction medium, reducing access to the active sites [5].



Figure 4: Ester content of biodiesel obtained with K/Fe(II)@Fe(III): (A): exposed to air for 3 h to 48 h. (B): with different oils with different FFA content, (C): in the presence of different H<sub>2</sub>O contents in the reactor and (D): the reusability of K/Fe(II)@Fe(III) over six cycles. Reaction conditions: temperature: 70°C, reaction time: 1 h, amount of catalyst: 10 %, stirring speed: 300 rpm, oil/ethanol ratio: 1/9.

## IV. CONCLUSIONS

The aim of this research is to prepare a heterogeneous catalyst based on magnetic iron impregnated with alkali metal that is more reusable for biodiesel production. The heterogeneous K/Fe(II)@Fe(III) catalyst proved to be the most efficient with an ethyl ester content of 94.86 % in the first cycle. The preparation conditions were: calcination temperature at 400°C, duration of calcination at 2 h, and impregnation ratio at 1/1. The catalyst also remained effective in the presence of an oil with a FFA content of more than 2 % and an alcohol water content of 3 %. The catalyst is reusable over at least two cycles without post-treatment with a biodiesel ethyl ester content of over 90 %. However, the catalyst remains very sensitive to exposure to ambient air, with a drop-in activity after 3 h exposure. With a view to producing biodiesel on an industrial scale, biodiesel characterisation is therefore envisaged in order to compare its specifications with standard specifications.

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