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Chitosan-Mediated NiO with Green Alkali for Hydrogenation of Soybean Oil: A New Compositional Discovery

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Abstract

This study investigated the chitosan-mediated (C-M) synthesis of C-M NiO (using banana peel ash as green alkali source), its composition and application as catalyst in the hydrogenation of soybean oil. C-M NiO was synthesized from the reaction of equal volumes (10 ml) of 0.01 M $NiSO_4.7H_2O$, ash filtrate and chitosan solution (0.1 g of chitosan in 100 ml of distilled water); while the control (NiO) was done without chitosan solution. Both catalysts were applied separately in the hydrogenation of soybean oil (*n*-hexane extract of dry soybean seed) under optimal condition with hydrogen gas and the products characterized with gas chromatography-mass spectrometric method (GC-MS). Characterization of the catalysts with X-ray diffraction (XRD) revealed mixed phase materials (majorly KCl/NiO, NiO and $Ni(OH)_2$) with broader peaks for the C-M NiO, while EDXRF confirmed the presence of K, Ni and Rb with higher intensities than those of C (graphite), Zn, Mg, Fe, Br and Cl. Also, AAS was used to quantify Ni and K (major elements from EDXRF). The results gave mean $[Ni^{2+}]$ and $[K^+]$ as 11.87 ± 0.32 and 90.35 ± 0.03 mgL^{-1} for C-M NiO but relatively higher concentrations of 14.86 ± 0.63 and 99.73 ± 0.06 mgL^{-1} respectively were obtained for NiO. SEM showed wider porous or multichannel skeletal polycrystallite networks for C-M NiO than NiO. GC-MS results indicated huge reduction in linoleic acid (dominant unsaturated fatty acid) from 55.12% to 7.54% for NiO and from 55.12% to 0% for the C-M NiO respectively, while stearic acid (saturated) increased from 4.55% to 46.18% for the control and 4.53% to 65.48% for the C-M NiO due to enhanced selectivity and catalytic conversion of unsaturated bonds to single bonds by the catalysts. Compositionally, the catalysts were confirmed to be K-major and were tagged KCl/NiO (K-rich) and C-M KCl/NiO (K-rich) respectively.

Key words: Soybean oil; Hydrogenation; AAS; Chitosan-mediated-KCl/NiO; banana-peel

1. INTRODUCTION

Nickel catalysts (raney, skeletal or finely divided) are particularly important in hydrogenation processes in organic reactions involving unsaturated hydrocarbons. The mechanism of nickel catalytic activity could be linked to its ability to initiate surface alkyl bond with unsaturated molecule (chemisorbs) that would desorb to saturated alkanes in the presence of hydrogen molecule, H_2. This surface acid catalyzed reaction active sites are also formed on its oxide, NiO surface when doped with a group IA (M) metal oxide like Li_2O in oxygen atmosphere due to the formation of a rare Ni^{3+} oxidation state, $Mx(Ni^{2+})_{1-2x}(Ni^{3+})_xO$, a strong Lewis acid [1].

Hydrogenation is a reduction process applied in petroleum and vegetable oil industries. It involves the reaction of hydrogen with unsaturated organic groups in the starting materials to produce partially or fully saturated forms of these groups. Vegetable oil hydrogenation processes could lead to the production of vegetable tallow, margarines, vegetable fats, and other components such as emulsifiers, soaps, creams, pastes, and similar substances for the cosmetic and chemical industries. Other domestic uses like frying and shortenings are also inclusive [2,3]. It increases the oxidative stability, improve the melting characteristics of the solid fat content, shelf-life and enhances the utility of the oil. The composition of the product is often affected by factors such as pressure of hydrogen, type of catalyst used, concentration, and agitation of the oil [4-5].

Catalysts commonly used include copper chromite, cobalt, nickel, and the noble metals. Others

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also reported in literature are CuO & CuO:H [6], Cu/SiO_2 [7], 8% Cu/SiO_2 [8], Ni/Al_2O_3 [9] and hydrogenated C-M CuO synthesized with green alkali [10]. The content of green alkali (from banana peels) besides KOH as major component, may include elements like Mg, Ca, Na, Fe, Ru, Br, Sr, Zr and Nb in decreasing order of percentage composition [11]. The presence of these metal impurities could enhance or inhibit the catalytic activities of compounds precipitated using green alkali from banana peels but their concentration in such catalysts have not been determined.

Previous reports have shown hydrogenation with CuO (precipitated using green alkali) as catalyst and a further enhancement with hydrogenated C-M CuO. However, none of these reports determined the composition of the synthesized metal oxide catalysts from green alkali (aqueous extract of plantain peel ash) spectrophotometrically to ascertain the associated K content relative to the analyte concentration. In addition, the use of KCl/NiO (K-rich) in the hydrogenation of Soybean oil has not been reported [11, 15].

Controlled crystallization of nickel oxide could lead to the formation of nano nickel oxides which exhibit better catalytic, electrical and magnetic properties that enhance their applications in dye-sensitization, photocathode, catalysis and magnetic materials. Nano nickel oxide catalyst and pure transition metals are conveniently synthesized by sol-gel method at low temperature with relatively high specific surface area. The methods of synthesis include but not limited to ultrasonic radiation, hydrothermal synthesis, precipitation-calcination and sol-gel [12]. Despite the sensitivity of the sol-gel method to moisture, the method has become versatile and important for the fabrication of nanostructured materials and making of advanced materials [13]. Some green sources of gels commonly used are chitosan, aloe-vera, agarose, starch and dextran [14]. Chitosan is a biodegradable polysaccharide derived from chitin which is found in crustaceans (shrimps, carbs, crayfish and lobster). It is soluble in water below pH of 7.0. Chitosan solution forms a poly-ion complex (gel) with anionic hydrocolloid. This property is often exploited in its sol-gel applications [15].

Soybean oil is an oil derived from the seeds of soybean which contains essential fatty acids. The oil is composed of 61% polyunsaturated fatty acids, having 53.2% linoleic acid and 7.8% linolenic acid, 24% monounsaturated fatty acid and 15% saturated fatty acid [16]. The unsaturated fatty acid component of soybean oil makes it a suitable substrate for checking the catalytic activity of chitosan mediated KCl/NiO (K-rich) in the hydrogenation of vegetable oil. The synthesis, application and (K & Ni) compositional analysis of KCl/NiO composite precipitated from nickel salt solution with green alkali and its C-M variant in the hydrogenation of soybean oil are investigated in this work. The findings would help to provide a cheaper and greener method of producing and functionalizing nickel oxide-based catalysts for hydrogenation reactions in the oil industries.

2. MATERIALS AND METHOD
2.1 Extraction of the Alkali from Ripe Banana Peels

Banana peels were collected from household waste. The peels were washed, chopped into smaller sizes, sun dried and milled. Thereafter, 179.254 g of the milled peels were heated to ash in a muffle furnace at 550 $^{\circ}$C for 6 h. The ash was removed from the furnace and cooled in a desiccator. Percentage ash content was determined using eq. 1

$$\% \ Ash \ = \ \frac{Ash \ wt.}{Sample \ wt.} \ \times \ 100 \qquad\qquad 1$$

The resultant ash (27 g) was dissolved in 365 ml of distilled water in a 500 ml volumetric flasks and was allowed to settle for 48 h to completely extract the green alkali (soluble bases) completely. The mixture was filtered using fitter paper and the concentration of alkali was titrimetrically determined (using 1M HCl acid solution with methyl orange as indicator) as 0.546 M.

2.2 Synthesis of chitosan-mediated KCl/NiO

Chitosan-mediated KCl/NiO was synthesized by dissolving 700 mg of nickel sulphate heptahydrate ($NiSO_4.7H_2O$) in 250 ml distilled water. Into two crucibles (one empty and the other containing 10 ml chitosan solution) were 10 ml of 0.01 M $NiSO_4.7H_2O$ each introduced, followed by the addition of 10 ml of the green alkali (MOH) with stirring. The resultant precipitates were oven dried (overnight) at 80 $^{\circ}$C leaving semi-solid substance which was transferred to a muffle furnace for ashing at 550 $^{\circ}$C for 5 h. It should be noted that the green alkali was later found to be the source of K and halides in the NiO produced upon characterization.

2.3 Structural and Elemental Analysis

Structures of the products were analyzed using the X-ray diffraction technique with EMPYREAN XRD Diffractometer operating with a generator voltage of 40 kV, current (40 mA), Cu anode Kα1 wavelength of 1.54 Å, 2-theta range (5-75 °C) and a step size of 0.0263. The product was ground and placed on a sample holder before slotting into the sample racket for analysis. Elemental composition and surface morphology were investigated using Energy Dispersive X-ray Florescence (EDXRF) and Scanning Electron Microscopy (SEM) respectively to identify all the elements present including non-crystalline phases and the surface morphology if multiphasic. The XRF spectrometer used was ARL QUANT'X EDXRF

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analyzer (9952120) from Thermo Fisher Scientific, Switzerland. A portion (0.5 g) of the samples were digested separately with 20 ml of aqua regia and made up to 100 ml with distilled water. Thereafter, an aliquot was aspirated into the Atomic Absorption Spectrometer (Agilent 4210 Microwave Plasma Atomic Emission Spectrometer) for the determination of $[Ni^{2+}]$ and $[K^+]$ contents of each catalyst.

2.4 Extraction of Soybean Oil

Soybean seeds were first selected by picking off dirt and stones and were oven dried at 105 °C for 7 h to remove moisture. The dry seeds were gently milled in a milling machine to dehull them. The dehulled seeds were further milled to powder form to increase the surface area for extraction of oil; and the oil was extracted through solvent extraction using *n*-hexane.

2.5 Hydrogenation of the Oil

Soybean oil (3 g) was weighed and dissolved in 18 ml of anhydrous tetrahydrofuran (THF) and the solution was transferred into a two-neck round bottom flask containing 300 mg of the (KCl/NiO or C-M KCl/NiO) and stirred. The reaction proceeded at room temperature with stirring under constant flow of hydrogen gas for 1 h. The mixture after the reaction was filtered and the hydrogenated oil collected for analysis.

2.6 Characterization of the Oil

Hydrogenated and un-hydrogenated soybean oil was characterized for its fatty acid profile using Gas Chromatography-Mass Spectrophotometric method [17]. The method involved the extraction of fatty acids from the oils using a mixture of methanolic NaOH, *n*-hexane and distilled water. The upper organic phase was separated and analyzed with the chromatograph (Agilent 7890A-USA) coupled with flame-ionization detector (FID) unit. Schematics of the methodology is shown in the graphical abstract (**Figure 1**).

Figure 1 Graphical abstract showing the various steps involved in the procedure

3.0 RESULTS AND DISCUSSION
3.1 Structural Characterization

The XRD reflection patterns of C-M KCl/NiO and KCl/NiO (control) crystallized from green alkali (K-rich) showed the presence of KCl (sylvite), dolomite and Graphite-2H indexed to American Mineralogist Crystal Structure Database (AMCSD) file nos. 96 (900-3130; 900-3524 and 101-1061) respectively [18-20]. The corresponding peaks of highest intensities for these phases were at 2-theta 28 °, 31 ° and 26 ° respectively (**Figure 2**). NiO was indexed to Joint Committee on Powder Diffraction Standards (JCPDS) card no.47-1049 [21].
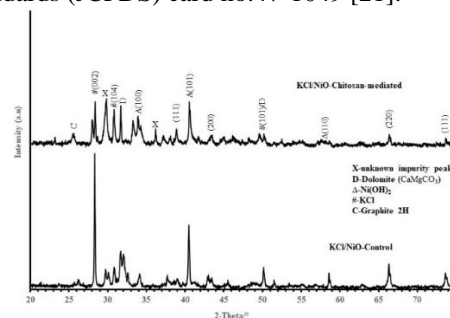

Figure 2 XRD patterns of KCl/NiO (control) and C-M KCl/NiO respectively showing reflections of NiO and other associated phases (labelled with symbols).

Broader peaks and lower intensities observed on the reflection patterns of C-M KCl/NiO was due to reduction in particle size and increase in porosity that characterized sol-gel synthesized samples as reported previously [10]. The presence of impurity peaks other than KCl/NiO was likely due to the elemental composition of banana peel ash, thus further analysis of the control and sample was done. The SEM showed white patches indicative of impurities (other phases) in the mist of the larger granular polycrystallites (**Figure 3a and 3c**). This was confirmed by EDXRF which showed the presence of K, Ni and Rb (major peaks) while C (graphite), Mg, Fe, Br and Cl were minors in KCl/NiO but Zn peak appeared on C-M KCl/NiO spectrum (**Figure 3b and 3d**). It should be noted that the same stock was used for C-M KCl/NiO synthesis. Chitosan (largely carbon chain) was eliminated upon carbonization leaving the catalyst with wider porous/multichannel skeletal polycrystallite networks as shown on the SEM micrograph of **Figure 3c** [10, 13]. The actual $[Ni^{2+}]$ and $[K^+]$ contents of the catalysts as determined spectrophotometrically were 11.87 ± 0.32 and 90.35 ± 0.03 mgL^{-1} for the C-M KCl/NiO and higher concentrations of 14.86 ± 0.63 and 99.73 ± 0.06 mgL^{-1} respectively were obtained for the KCl/NiO-control sample (**Table 1**). This was necessary to confirm the stronger K peaks on both EDXRF spectra. The AAS result also supported the lower reflections (intensities) of peaks observed on the EDXRF and XRD for the C-M KCl/NiO as compared to the control (KCl/NiO).
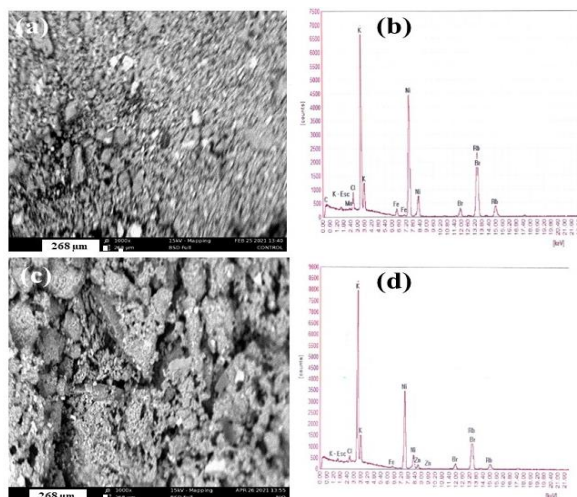
Figure 3 SEM micrograph and EDXRF spectrum of
(a,b) KCl/NiO and (c,d) C-M KCl/NiO

3.2 Characterization of the soybean oil and the hydrogenated oils

Fatty acid compositions of soybean oil and the hydrogenated soybean oils are shown in **Table 2**. Distribution and percentage of fatty acid in soybean oil showed that the oil has 87.16% total unsaturated fatty acids of which linoleic acid dominated with 55.12%, and 13.71% total saturated fatty acid with Palmitic

acid dominating with 6.73%. However, upon hydrogenation the total unsaturated fatty acids decreased from 87.16% to 77.93% for the KCl/NiO (control) catalyzed oil and 87.16% to 29.33% for the C-M KCl/NiO catalyzed oil. On the other hand, total saturated fatty acids increased significantly from 13.71% to 76.71% for KCl/NiO (control) and 13.71% to 70.62% for C-M catalyzed oil. Lower content of saturated fatty acids in C-M catalyzed oil might be due to increased isomerization during hydrogenation to monounsaturated product. It was observed that polyunsaturated fatty acids were eliminated by the C-M catalyst but higher concentration of Palmitoleic ($C_{16.1}$-monounsaturated), absent in the soybean oil was formed after hydrogenation by both catalysts with C-M having greater concentration of 13.50% (Table 1). This result agreed with similar observation reported for the formation of new compounds (including increase in palmitoleic acid) during the catalytic hydrogenation of cashew kernel oil due to isomerization [6]. Only the C-M KCl/NiO catalyst reduced oleic acid ($C_{18.1}$) concentration while the control had no effect on the oleic acid double bond rather it catalyzed the formation of more oleic acid as hydrogenated products. Such level of selectivity of C-M KCl/NiO over KCl/NiO catalyst was quite significant.

Table 1: Concentrations of Ni and K in the control and C-M samples in ppm

Sample	[Ni]	[Ni]	[Ni]	Mean+SD[Ni]	[K]	[K]	[K]	Mean+ SD [K]
NiO	14.86	14.24	15.49	14.86 ± 0.63	99.73	99.67	99.79	99.73 ± 0.06
NiO-CHT	11.87	11.54	12.17	11.87 ± 0.32	90.35	90.38	90.33	90.35 ± 0.03

Table 2: Fatty Acid Composition in Soybean and Hydrogenated Soybean Oils

Fatty Acid	% Composition before Hydrogenation	% Composition after Hydrogenation	
		KCl/NiO (control)	KCl/NiO (chitosan-mediated)
Myristic acid $C_{14.0}$	0.49	0.64	0.84
Palmitic acid $C_{16.0}$	6.73	2.18	0.72
Palmitoleic acid $C_{16.1}$	-	1.30	13.50
Stearic acid $C_{18.0}$	**4.53**	**46.18**	**65.48**
Oleic acid $C_{18.1}$	24.04	44.23	15.83
Linoleic acid $C_{18.2}$	**55.12**	**7.34**	**-**
Linolenic acid $C_{18.3}$	8.00	1.23	-
Arachidic acid $C_{20.0}$	0.96	27.71	1.34
Paullinic acid $C_{20.1}$	-	0.77	-
Eicosadienoic acid $C_{20.2}$	-	1.10	-
Dihomo-y-linolenic acid $C_{20.3}$	-	21.96	-
Behenic acid $C_{22.0}$	0.50	-	-
Lignoceric acid $C_{24.0}$	0.50	-	-
Total saturated	**13.71**	**76.71**	**70.62**
Total unsaturated	**87.16**	**77.93**	**29.33**
Monounsaturated	24.04	46.3	29.33
Polyunsaturated	63.12	31.63	-

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The GC-MS chromatograms of the oils are shown in **Figure 4**. Fatty acid composition and distribution in the soybean oil agreed with literature [16]. The observed reduction or elimination of some peaks was due to the addition of hydrogen to the unsaturated fatty acids across the double or triple bonds to form single bonds (saturated fatty acids). Thus, significant reduction in the dominant unsaturated fatty acid (linoleic acid) concentration from 55.12% to 7.34% and to 0% for the KCl/NiO and C-M KCl/NiO catalysts respectively were observed upon hydrogenation. Conversely, stearic acid (saturated) increased from 4.53% to 46.18% for KCl/NiO (control) and to 65.48% for C-M KCl/NiO catalyzed soybean oil. From the result obtained, C-M KCl/NiO catalyst gave better hydrogenation result compared to that of the control. This effect was attributed to size reduction and addition of pores or multichannel by the chitosan template during calcination (heating of the catalyst in the furnace) [10]. The result also showed higher linoleic, linolenic and polyunsaturated acids selectivity by C-M KCl/NiO catalyst than the control.
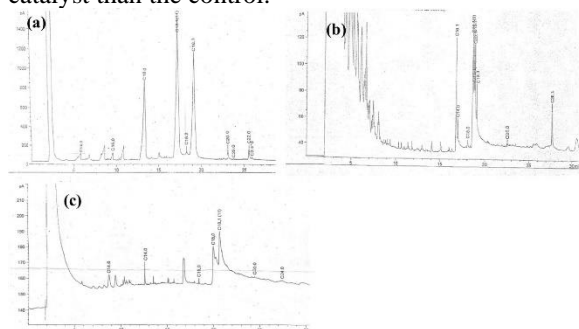

Figure 4 GC-MS of (a) Soybean Oil (b) Hydrogenated soybean oil over KCl/NiO and (c) Hydrogenated Soybean over C-M KCl/NiO catalysts

4. CONCLUSION

Chitosan-mediated KCl/NiO was successfully synthesized using a green alkali (filtrate of banana peel ash) and applied as catalyst for the first time in the hydrogenation of soybean oil. Compositional investigation of the C-M KCl/NiO catalyst revealed that it consists largely of KCl. XRD confirmed mixed phase composites (containing majorly KCl/NiO, NiO and Ni(OH)$_2$) for the catalysts and particle size reduction for C-M KCl/NiO. Hydrogenation of unsaturated fatty acids of soybean oil using the catalysts was effective. C-M KCl/NiO composite completely converted the dominant linoleic, linolenic and polyunsaturated fatty acids to saturated fatty acids and exhibited higher selectivity over KCl/NiO. Therefore, C-M KCl/NiO is recommended for use in hydrogenation reactions.

5. ACKNOWLEDGEMENTS

6. COMPETING INTERESTS

The authors declare that there is no conflict of interest over this work. No funding was received for the conduct of this study from any other body except contributions by the authors.

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