STUDIES OF NEAT KAOLIN AND COBALT (III) OXIDE DOPPED KAOLIN FOR HETEROGENEOUS CATALYSTS DEVELOPMENT USING FOURIER TRANSFORM INFRARED SPECTROSCOPY

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ABSTRACT
Mesoporous Co_3O_4/kaolin as a potential heterogeneous catalyst was prepared by the method of impregnation and its infrared spectroscopic absorption was recorded from 4000 – 650 cm^{-1} and the resultant peaks obtained were compared with the infrared absorption peaks of the neat kaolin that was used to prepare the former and also the infrared spectra of Co_3O_4 on various clay minerals found on the related literatures. The result of the analyses indicated two sharp absorption bands at 3688 cm^{-1} and 3623 cm^{-1} on both the spectra of the neat kaolin and that of the Co_3O_4/kaolin. However, the two sharp peaks were observed to have decreased intensities on the spectrum of the latter, probably due to the effect of doping the kaolin with cobalt nitrate hexahydrate and the subsequent thermal treatment it undergoes. The spectrum of the Co_3O_4/kaolin was observed to have developed a broad absorption band from 3650-3200 cm^{-1} associated with the bending and stretching vibrations of the hydroxyl groups of the chemisorbed water molecules attached to the Co_3O_4/kaolin. The peak on the spectrum of Co_3O_4/kaolin at 1334 cm^{-1} is associated **with** the stretching vibrations of C–O and also the medium peak at 739 cm^{-1} is due to the vibrations of Co(III)-O bonds, and these two peaks confirmed the formation of cobalt oxide kaolinite bond, and this bond between the cobalt oxide and the kaolinite that actually enhances the catalytic ability of the kaolinite and also to have heterogenized the oxides of cobalt that was produced on thermal treatment of the cobalt (ii) nitrate hexahydrate doped kaolin.

**Keywords:** Kaolin, Peak, Spectroscopy, Band, Absorption.

INTRODUCTION:
Fourier-transform infrared spectroscopy (FTIR) is a technique used to obtain an infrared spectrum of absorption or emission of solids, liquids or gaseous particles. FTIR spectroscopy is commonly used to characterize specific adsorbates and because of the localized nature and particular chemical specificity of molecular vibrations, its spectra are quite rich in information and it can be used to infer both structural and compositional information on the adsorbate and as well as on its coordination on the surface of the catalyst. In some instances, the technique is also suitable for the direct characterization of solids, especially if they can be probed in the far-IR region. The technique works on the basis of functional groups and provide information in the form of peaks. The technique shines a beam containing many frequencies of light at once and measures how much of that beam is absorbed by the sample, and next, the beam is modified to contain a different combination of frequencies to give a second data point. A number of reactions catalysed by acids and bases in solutions can also be catalysed by solids having acidic and basic properties, solid acid catalysts usually employed are mixed oxides, zeolites and clays, the high specific surface area, chemical and mechanical stability, layered structure, high cation exchange capacity (CEC), Bronsted and Lewis acidity, etc., have made the clays excellent materials for adsorption (Tanabe, 1981).

Catalysis started to play a major impact in the chemical industries starting from the beginning of the twentieth century and nowadays more than 95% of chemicals are produced via one or more processes that involve one or more catalytic steps. Heterogeneous catalysts are commercially used as catalysts due to their extensive applications such as adsorption and large surface area. The use of kaolin as the catalyst support is due to its ability to heterogenized some homogeneous catalysts. This is aimed at producing heterogeneous catalysts from cheap and locally sourced materials so as to reduce the cost of importation and to help boost the local chemical industries which rely on the use **of** catalysts for chemical processes in the production of goods. Cobalt nitrate is an inorganic compound with the chemical formula of $Co(NO_3)_2 \bullet xH_2O$. It is a salt of cobalt and the most common form of it is the hexahydrate form having the chemical formula of $Co(NO_3)_2 \bullet 6H_2O$, it is a reddish-brown deliquescent salt that is soluble in water and other polar solvents. Cobalt nitrate supported on Al_2O_3 dehydration proceeds in three stages, it usually starts at about 40 °C and is completed at 140 °C, that is temperature of 35 °C lower than the final dehydration temperature of the bulk cobalt nitrate. The nitrogen oxide produced begins to evolve after the dehydration of the salt completes at 140 °C which is the temperature about thirty-five degrees lower than the dehydration of the bulk cobalt nitrate. Though traces of nitrogen oxides evolved during the dehydration, similar to what was observed for the bulk cobalt nitrate. The decomposition of supported cobalt nitrate is usually terminated at about 210 °C. The final product of the bulk cobalt nitrate decomposition is Co_3O_4 as confirmed by XRD analysis and stays in agreement with the results presented in the literature (Malecka *et al.,* 2014). The decomposition of cobalt nitrate supported on Al_2O_3 leads to $CoAl_2O_4$ spinel as the final product at a temperature of 210 °C. The equation for the thermal decomposition of

$Co(NO_3)_2 \bullet 6H_2O$ is given in eqn. 1

$$3Co(NO_3)_2 \bullet 6H_2O_{(s)} \longrightarrow Co_3O_{4(s)} + 6NO_{2(g)} + 6H_2O_{(g)}$$
....Eqn.1
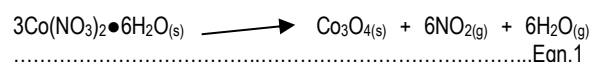
Thermal decomposition of cobalt nitrate to produce cobalt (ii) oxide, nitrogen dioxide and oxygen, the reaction takes place at a temperature near 1000°C in an atmosphere of nitrogen gas. It is commonly reduced to metallic high-purity cobalt at such elevated temperatures; therefore, it can be adsorbed onto various catalyst supports for use in Fischer-Tropsch reactions. Cobalt (ii) oxide is an inorganic compound that has been described as an olive-green or gray solid, it is a family of chemical compounds consisting of cobalt and oxygen atoms and compounds in the cobalt oxide family **including** cobalt (ii) oxide (CoO) commonly called cobaltous oxide, cobalt (iii) oxide (Co_2O_3) commonly called cobaltic oxide and cobalt (ii, iii) oxide having the chemical formula of Co_3O_4 (John and Detmar, 2005).

MATERIALS AND METHODS:
The laboratory apparatus used in this research are listed on Table 1

Table 1: List of Apparatus

S/No.	Equipment	Model	Manufacturer
1.	Weighing Balance	Adventurer, AR 3130	OHAUS, China.
2.	FTIR Spectrometer	Cary 630 FTIR	Agilent technologies
3.	Muffle Furnace	MF 207	NÜVE SANAYI, TURKEY
4.	Ultrsonicator	DR-LQ20	Derui Ltd.
5.	Drying oven	DHG-9023A	Surgifriend Medics, England

Table 2: List of reagents

S/No:	Reagent	Formula
%Purity	Manufacture	
1	Cobalt (ii) nitrate hexahydrate	$CoO(NO_3)_2.6H_2O$
99%	Merck	

Sample collection and treatment
Kaolin sample was collected from a kaolin **quarry** site in Kankara town of Kankara Local Government area of Katsina State on the geographical coordinates of 11°55'47" N × 7°25'11" E following the literature methods (Atta *et al.,* 2007; Jide, 2014 and Hadi *et al.,* 2016).
A clean shovel was used to dig a v-shaped hole of 20 cm depth at each sampling point then a slice of the kaolin was taken and stored in a clean glass bottle, eight sub-samples (100g) each per hectare were taken to form one composite sample and the depth at which the sub-samples were taken range from 2 to 20 cm. The composite samples were inserted into clean glass containers each and labelled as A1, A2, A3, A4, A5, A6, A7, and A8 respectively, after which, they were transported to the laboratory. In the laboratory, each composite sample was grounded using a pestle and mortar. The samples were further combined to form one homogeneous composite sample that was subjected to a series of cone and quartering methods to obtain a representative sample of 200 mg that was pulverized again and then sieved through 2 mm mesh sieve. The pulverized kaolin (100 g) was transferred into a 1000 cm^3 beaker containing 400 cm^3 distilled water and the mixture was stirred and allowed to stand for 1 hr after which it was decanted.

The washing was repeated two more times to remove suspended particles from the kaolin and the wet kaolin was oven dried at 105 °C for 12 hours the dried kaolin pulverized, sieved and then stored in a clean glass container for use.

Preparation of reagent
The 0.1252 M $Co(NO_3)_3$•$6H_2O$ used to prepare 20 wt% Co_3O_4/kaolin was prepared as follows:
77.6778 g of $Co(NO_3)_3$•$6H_2O$ salt was dissolved into a 500 cm^3 beaker containing 200 cm^3 of distilled water. The mixture was stirred until the salt dissolved and the solution was transferred into a 1000 cm^3 volumetric flask, the beaker was washed two more times with distilled water and the washings was transferred into the volumetric flask containing the solution and the volume of the solution was adjusted to 1000 cm^3 using distilled water.

Preparation of iron (iii) oxide on kaolin (Co_3O_4/kaolin)
The metal oxide on kaolin was prepared by impregnation method as follows:
100 g of the neat kaolin was transferred into a 1000 cm^3 beaker and 300 cm^3 of the prepared 0.1252 M solution of $Co(NO_3)_3$•$6H_2O$ was added to it and the mixture was stirred for 30 min, it was then ultrasonicated for 8 hrs. at 80 °C after which it was allowed to age for 24 hr. After aging the mixture was placed on a hot plate at 80 °C to evaporate the excess solvent, after which it was oven dried at 105 °C in an oven for 24 hrs. and the dried mass was pulverized using pestle and mortar and then sieved through a 2 mm mesh sieve.
The dried mixture of cobalt (ii) nitrate hexahydrate and kaolin was then calcinated, during the calcination process a given mass of the mixture was weighed and transferred into a crucible and the crucible and its contents were inserted into a muffle furnace that was set at 320 °C and the calcination was conducted for 2 hrs. The calcination product (Co_3O_4/kaolin) was allowed to cool to room temperature and then it was removed from the muffle furnace and the material was transferred into a corked clean sample bottle for analysis. A given mass of the sample was taken for Fourier transform infrared spectroscopic measurements, however, the neat kaolin was not subjected to the above treatment, rather, it was only subjected to the Fourier transform infrared spectroscopic measurements under the same condition with the cobalt (ii) nitrate hexahydrate treated kaolin.

Fourier Transform Infrared Spectroscopic analysis (FTIR) of the neat kaolin and the Co_3O_4/kaolin
The FTIR Analysis was done using an Agilent Cary 630 FTIR spectrometer with a base system of high emission of infrared radiation. The infrared spectrum of both neat the kaolin and Co_3O_4/kaolin samples was measured using attenuated total reflectance Fourier transform infrared spectroscopic analysis (ATR-FT-IR) using the method described by Reddy (2008) with slight modification by using 256 scans at a resolution of 4 cm^{-1} and placing 0.5 g of each sample and the base system was used in conjunction with 5 bounce diamond ATR sampling accessories of internal reflection element (IRE) crystal on the diamond sample holder and recording the spectrum of each sample in the range of 4000 – 650 cm^{-1}. The generation of the sample spectra was achieved through MicroLab software on a personal computer attached to the FTIR instrument.

RESULTS

The FTIR spectrum of the neat kaolin is displayed on Figure 1 and that of the Co_3O_4/kaolin is displayed on Figure 2.
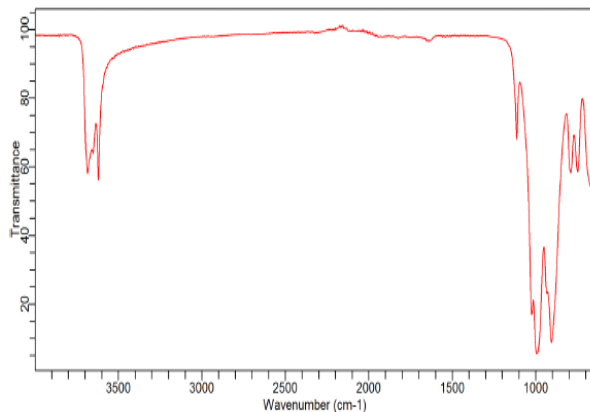

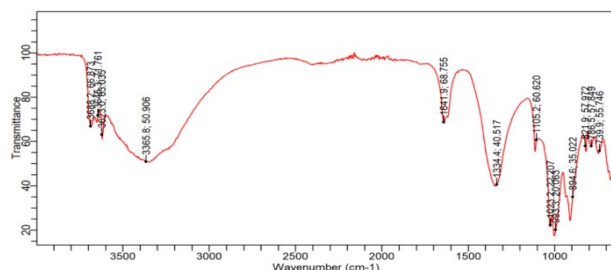**Figure 1:** FTIR spectrum of the neat kaolin

Figure 2: FTIR spectrum of the Co_3O_4/kaolin

Table 1: Absorption bands of the FTIR analysed neat kaolin and Co_3O_4/kaolin

S/No.	Frequency of absorption (cm⁻¹)	Intensity	Functional group	Vibration mode	Figure
1	3688	Sharp	OH	Stretching	1 and 2
2	3623	Sharp	OH	Bending	1 and 2
3	3650-3200	Broad	OH	Stretching	2
4	1641	Weak	OH	Bending	1
5	1641	Sharp	O-H	Bending	2
6	1334	Medium	Co-O	Stretching	2
7	1100	Sharp	Al-O	Bending	1 and 2
8	1020	Medium	Si-O	Stretching	1 and 2
9	993	Sharp	Si-O-Si	Bending	1 and 2
10	900	Weak	Al-O-Al	Stretching	1 and 2
11	821	Medium	Al-OH	Stretching	1 and 2
12	786	Medium	Si-O	Stretching	1 and 2
13	739	Medium	Co-O	Bending	2

DISCUSSION:

Figure 1 shows the FTIR spectrum of the neat kaolin, while, Figure 2 is the FTIR spectrum of the Co_3O_4/kaolin. Table 1 is the summary of the absorption bands for both the neat kaolin and the Co_3O_4/kaolin in the range of 4000 – 650 cm⁻¹. In both the two spectra, there appeared two sharp absorption bands at 3688 cm⁻¹ and 3623 cm⁻¹ these absorption bands are due to the stretching vibrations of the hydroxyl groups occupying the edges of the clay platelets and the surfaces of the octahedral layers and as well the internal hydroxyl groups that interact with the surface of the oxygen atoms of the adjacent tetrahedral layers (Zhang *et. al.,* 2012; Konan *et al.,* 2009). These absorption bands were observed to be present in both the neat kaolin and the Co_3O_4/kaolin, therefore, doping the neat kaolin with the $Co(NO_3)_3 \bullet 6H_2O$ and the subsequent calcination of the doped kaolin to produce the Co_3O_4/kaolin has not altered the structural arrangement of the neat kaolin at this level. The FTIR spectrum of the Co_3O_4/kaolin shows a broad absorption band from 3650 - 3200 cm⁻¹ this absorption band is chiefly associated with the bending and stretching vibrations of the hydroxyl groups of the chemisorbed water molecules attached to the Co_3O_4/kaolin since the latter is a hygroscopic substance (Zhang, 2012), however, this broad peak was observed to be absent on the FTIR spectrum of the neat kaolin. The weak absorption band at 1641 cm⁻¹ on the FTIR spectrum of the neat kaolin and similarly, this peak appeared to be very sharp at the same point on the FTIR spectrum of the Co_3O_4/kaolin and these peaks are attributed to the bending vibrations of the physiosorbed water molecules within the matrix of the neat kaolin and the Co_3O_4/kaolin (Aboelazm *et al.,* 2018; Obazee *et al.,* 2018).

The band at 1334 cm^{-1} is associated to the stretching vibrations of C–O (Xu *et al.,* 2014) and this peak only appeared on the FTIR spectrum of the Co$_3$O$_4$/kaolin but absent on the FTIR spectrum of the neat kaolin, therefore, this peak can be associated to the cobalt oxide kaolin linkage in the form of Co-O-kaolin. The mild peak appearing at 1100 cm^{-1} on the spectra of both the neat kaolin and that of the Co$_3$O$_4$/kaolin are due to the stretching and bending vibrations of Al-O on the octahedral layers of the kaolin.

The medium peak at 1020 cm^{-1} and the sharp peak at 993 cm^{-1} are associated to the stretching vibrations of the apical Si-O (Mustapha *et al.,* 2020), while, the sharp peak appearing like a shoulder at 900 cm^{-1} is associated to the Si-O-Si stretching vibrations. The medium peak at 821 cm^{-1} is attributed to vibrations of Al-O-H sitting at the surfaces of the alumina and as well as the Si-O-Al vibrations and more or less to the hydroxyl groups perpendicular to the surface which are popularly known as translational OH groups (Farmer and Russell cited in Konan *et al.,* 2009; Saikia, 2010). The medium peak appearing at 786 cm^{-1} is chiefly due to the stretching vibration of the Si-O bond mostly found in clay minerals such as quartz as it is one of the minerals present in kaolin (Saikia, 2010) and the medium peak at 739 cm^{-1} is due to the vibrations of Co(III)-O bonds (Aboelazm *et al.,* 2018). However, the absorption bands associated with the kaolinite mineral observed on the FTIR spectrum of the neat kaolin were observed to have decreased intensities on the FTIR spectrum of the Co$_3$O$_4$/kaolin. This decrease in intensities is associated with the thermal treatment to which the cobalt (ii) nitrate hexahydrate doped kaolin was subjected to produce the Co$_3$O$_4$/kaolin, a similar scenario has also been observed on the FTIR spectra of [Co(NH$_3$)$_4$CO$_3$]NO$_3$●H$_2$O and its decomposition products (Farhadi *et al.,* 2013). The peak on the spectrum of Co$_3$O$_4$/kaolin at 1334 cm^{-1} is associated to the stretching vibrations of C–O and also the medium peak at 739 cm^{-1} is due to the vibrations of Co(III)-O bonds, and these two peaks confirmed the formation of cobalt oxide kaolinite bond and this bond between the cobalt oxide and the kaolinite that actually enhances the catalytic ability of the kaolinite and also to heterogenized the oxides of cobalt that will be produced on thermal treatment.

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Studies OF Neat Kaolin And Cobalt (III) Oxide Dopped Kaolin For Heterogeneous Catalysts Development Using Fourier Transform Infrared Spectroscopy.

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