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CATALYST DEVELOPMENT FROM LOCALLY AVAILABLE RESOURCES - (A CASE STUDY OF NICKEL-SILICA CATALYST)

BY

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A RESEARCH PROJECT SUBMITTED TO THE DEPARTMENT OF PURE AND INDUSTRIAL CHEMISTRY, FACULTY OF PHYSICAL SCIENCES, UNIVERSITY OF NIGERIA, NSUKKA, IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF MASTER OF SCIENCE (M.Sc.) DEGREE IN PHYSICAL CHEMISTRY.

DECEMBER, 2014.

DECLARATION

This project titled ñCatalyst Development from Locally Available Sourcesò was carried out by me and has not been presented in any previous application for any degree or diploma and all the literature cited were duly acknowledged in the references.

OBIEKWE, CLARA AMALACHI ______________________

CERTIFICATION

This is to certify that OBIEKWE CLARA AMALACHI, a Postgraduate student in the Department of Pure and Industrial Chemistry with registration number PG/M.Sc./12/62633, has satisfactorily completed the requirements of research work for the award of Master of Science (M.Sc.) degree in Physical Chemistry. This research work is original and has never been submitted in part or whole for any other diploma or degree in this or any other University.

Prof. L. E. Aneke
Project Supervisor
Date: ....

Dr. A. E. Ochonogor
Head of Department
Date: ....

DEDICATION

This research work is dedicated to God who never fails.

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ABSTRACT

The efficacy of silica obtained from our local sand as a carrier in synthesis of Nickel-Silica catalyst was investigated. Six samples of soil were collected from two different sites (comprising five white coloured samples collected from Iva valley, lower part of Milliken hill, namely: pottery 2 (P2), down iva (DI), run-off iva (ROI), pottery rock (POR), white chalk (WTC) and one brown coloured sample (UdS) collected from Udi Siding) in Enugu, Nigeria. Prior to treatment by flotation method, some properties that could affect their catalytic use like organic matter content, texture, porosity and pH were assayed. (i) P2 (pH, 4.7; fine sand, 74.29 %; organic matter, 0.26 %), (ii) DI (pH, 4.7; fine sand, 72.72 %; organic matter, 0.26 %), (iii) ROI (pH, 7.4; fine sand, 87.42 %; organic matter, 0.19 %), (iv) POR (pH, 6.4; fine sand, 85.65 %; organic matter, 0.0%), (v) WTC (pH, 4.7; fine sand, 83.59 %; organic matter, 0.07 %) and (vi) UdS (pH, 4.4; fine sand, 32.79 %; organic matter, 0.19 %). Three of the samples with the best results ROI, POR, and WTC as can be seen above were selected. The pre-treated sand was purified by leaching process using 20 % HF, 20 % H_2SO_4, 10 % NaOH and distilled water. Comparison of the XRD results of the raw sand sample and silica extract showed complete removal of Al, Ca, and other oxide impurities from the raw sand. The silica was coupled with nickel employing two catalyst preparation methods. The Deposition method was used to couple silica with $Ni(NO_3)_2$ to prepare the catalyst named DPNN and $NiCl_2$ to prepare the catalyst named DPNC. In the Co-precipitation method, silica was coupled with $NiCl_2$ to prepare the catalyst named CPNC. The surface area, pore volume and particle size distributions of the catalyst samples were determined by N_2 adsorption at 77 K using Trister II Plus BET analyzer. The elemental composition was obtained by XRF spectroscopy. Effect of using two different nickel precursors for coupling was investigated; the result showed that $NiNO_3$ gave a higher degree of Ni dispersion and incorporation compared to $NiCl_2$. Effect of using two different catalyst preparation methods was also investigated; Co-precipitation method allowed the highest degree of Ni incorporation and improved surface properties. The results showed that Ni-silica catalysts prepared using silica from the local soil has catalytic properties that are similar to the standard Ni-Silica catalyst, Euro Ni-1, and better catalytic properties than some previously synthesized ones reported by Unichema, C. B. V. (1990), Wang, W. *et al* (2006), and Hermida, L. *et al* (2012).

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CHAPTER ONE

1. INTRODUCTION

1.1 BACKGROUND OF STUDY

The search for catalysts or improved catalysts seems to be a never ending one since small reductions in operating temperature and pressure, or small differences in yields or product distribution affected by catalysts can have great economic importance on the commercial scale.

Catalysts are chemical substances that modify the rate of a chemical reaction, usually by acceleration; while catalysis is the process in which the rate of a chemical reaction is influenced by a catalyst[1,2]. Examples of catalysts include hydrogen ion, Vanadium (v) Oxide, nickel etc. Industrial catalytic processes includes: hydrogenation of oils, Ammonia synthesis, cracking of petroleum, Friedel Crafts reaction etc.

In most cases, industrial catalysts contain 3 groups of components: catalytically active materials, catalyst support and promoters. Catalytically active material is a precursor to industrial catalyst; they possess appropriate catalytic properties (activity and selectivity) but still do not have the complex of properties required for industrial catalyst. The complex of properties include proper pore structure, long lifetime, high resistance to deactivation and poisons, easy regeneration, low operating temperature, high thermal stability, high mechanical strength, resistance to attrition and low price[3].

Sand is everywhere around us, not often used in the chemistry laboratory as it contains a lot of impurities. Adding value to sand by purification turns it into silicon dioxide which has many applications in chemistry. Furthermore, combination of silica with some catalytically active substances like alumina, nickel, platinum, copper etc makes it improved catalyst with better activity and evenly dispersion of the active agent on the carrier.

Improvements that may result from dispersion of the catalytically active agent include:

- Increase of available surface
- Stabilization against crystal growth and sintering
- Creation of a favourable orientation of surface molecules
- Improvement of mechanical strength

Nickel-silica catalysts have potential application generally for hydrogenation[4,5]; also in petrochemical industry for processes like deoxygenation, methanation, reforming, and hydro-cracking[6].

The existence of raw sand with proper composition and catalytic ability has been reported; the sand was treated and used to accomplish the catalysis of Friedel Crafts acylation[7].

Catalysts are employed in many industrial processes; special mention is made of the processes for the manufacture and upgrading of motor gasoline. This industry is by far the largest user of catalyst and has been the inspiration for much of the progress in the development of catalysts and the techniques of their manufacture and use[8].

Steps involved in catalyst development are as follows:

- Choice from previous knowledge, of the elements or compounds known to be effective in reactions of the type under consideration;
- Narrowing down by actual experimental test, of the list of possible catalysts to identify those that are most promising;
- Attempting to improve the performance of the catalysts selected by preparing and testing their mixture, by subjecting them to treatments designed to increase their specific surface area, by trying different activation methods, and by varying the size of the catalyst particles;
- Attempting to characterise the detailed form and structure, as well as the properties of the catalyst and to correlate them with the performance of the catalyst.

1.2 Statement of Problem

The use of imported catalyst is the order of the day. In our research lab; the small scale reactions employ expensive imported catalyst, likewise our chemical industries that produce in large scale.

Silica is cheap and readily available, but it is imported; intensive research on purifying our local soil and producing silica based products from it is needed to put our raw materials to use.

Although many efficacious catalysts exist and nickel-silica (Ni-SiO_2) has been synthesized[6], there is need to develop the best of the catalyst by trying different methods of preparation and comparing their products. Presently, no combined silica catalysts have been synthesized employing silica from our local soil, to the best of our knowledge.

1.3 Research Objectives

This work is aimed at:

- Testing different soil samples with the aim of selecting the sample with the best surface features for catalyst application;
- Purification of the samples using both physical means and chemical leaching into silica; this makes it suitable for application in many chemical industries/processes;
- Development of nickel-silica catalyst using silica from the locally available soils by co-precipitation and deposition methods;
- Physico-chemical characterisation of the prepared nickel silica catalysts; and
- Optimization of preparation method for the nickel-silica catalyst and comparing the effect of two nickel precursors on the final product.

1.4 Justification of the Study

The successes of basic research in the field of catalysis have direct effect on solving many fundamental problems that face humanity. Examples of such solutions include: efficient utilisation of raw materials, mastering of new sources of energy and improvement on the existing ones, and development of efficient systems for environmental protection[3].

Due to high cost of running high temperature engines coupled with the long duration of some chemical reactions, it becomes imperative to resort to use of catalysts to speed up such reactions. It is also unreasonable to import expensive and non-specialty catalysts while their alternatives could be synthesized locally.

CHAPTER TWO

2. LITERATURE REVIEW

2.1 Sand and Silica

Figure 2.1: Sandy soil (Source: Ref. 10)

Soil is a naturally occurring granular material composed of finely divided rock and mineral particles[10]. The composition of soil is highly variable, depending on the local rock sources and conditions in an environment, but the most common constituent of soil is silica (silicon dioxide, (SiO_2)), usually in the form of quartz which, because of its chemical inertness and considerable hardness, is the most common mineral resistant to weathering[11].

The second most common type of soil is calcium carbonate (limestone), for example aragonite, which has mostly been created by various forms of life, like coral and shellfish. It is, for example, the primary form of soil apparent in areas where reefs have dominated the ecosystem like the Caribbean.

The bright white soils found in tropical and subtropical coastal settings are eroded limestone and may contain coral and shell fragments in addition to other organic or organically derived fragmental material, suggesting soil formation depends on living organisms, too[12]. Some soils contain kaolin, magnetite, chlorite, glauconite or gypsum.

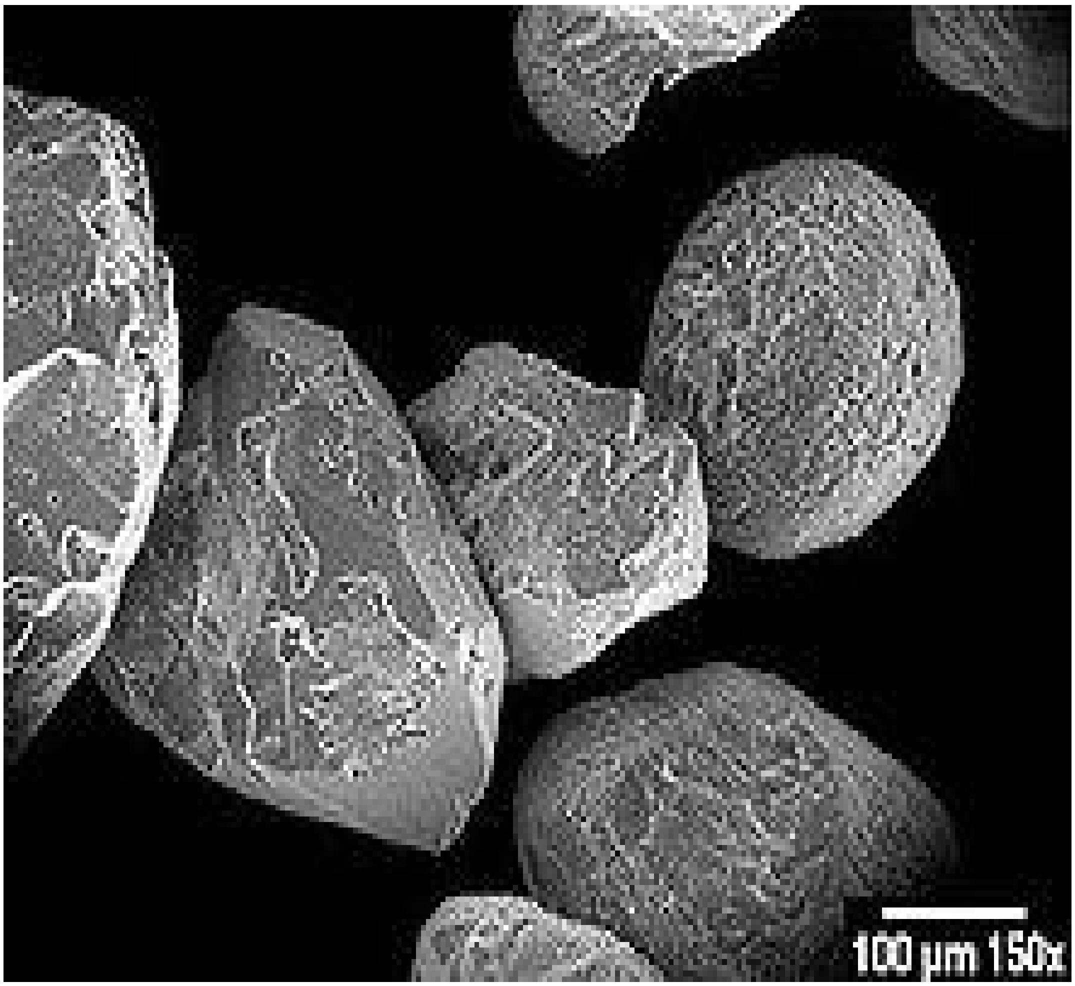

Figure 2.2: An electron micrograph showing grains of sand (Source: Ref. 13)

Kaolin is used in the manufacture of catalysts because the refractory character of kaolin is appropriate for catalysts used at high temperatures and pressures[14]. Refining of kaolin from the crude state enhances its whiteness, purity and other important commercial characteristics. The largest use of kaolin is in catalyst substrates in the catalytic cracking of petroleum[15]. The purity of the kaolin is critical in the petroleum cracking operation; so processed kaolin with low iron, titanium and alkali and alkaline earth compounds is preferred. It is estimated that over 200,000 tons of kaolin are used annually to produce petroleum cracking catalysts[15]. Kaolin is the most important raw material in producing zeolite as a catalyst used in Fluid Catalytic Cracking process[16,17], where kaolin modify the properties of catalytic cracking catalysts, such as reducing coke yield, improving attrition resistance, high tolerance to contaminated metal and high thermal stability[14]. Kaolins are excellent supports for Lewis acids or for transition metals applied in organic reactions like Friedel-Crafts, acylation and alkylation of aromatics[14].

Soil has a lot of applications to mention but a few: in agriculture, aquaria, beach nourishment, brick making and mortar in masonry construction, concrete, hydraulic fracturing, paint - mixing sand with paint produces a textured finish for walls and ceilings or non-slip floor surfaces, railroads-to improve the traction of wheels on the rails, recreation-playing with sand as in sand castles and sandboxes, water filtration- media filters use sand for filtering water as in sand bed etc.

In chemistry laboratory, a sand bath is a common piece of equipment made from a container filled with heated sand. It is used to provide even heating for another container, most often during a chemical reaction.

A sand bath is most commonly used in conjunction with a hot plate or heating mantle. A beaker is filled with sand or metal pellets (called shot) and is placed on the plate or mantle. The reaction vessel is then partially covered by sand or pellets. The sand or shot then conducts the heat from the plate to all sides of the reaction vessel. This technique allows a reaction vessel to be heated throughout with minimal stirring, as opposed to heating the bottom of the vessel and waiting for convection to heat the remainder; cutting down on both the duration of the reaction and the possibility of side reactions that may occur at higher temperatures.

Hazards

While soil is generally non-toxic, soil and silica-using activities such as glassmaking, sandblasting, etc require precautions like wearing a face mask, as it can irritate the throat and lungs if inhaled. Material safety data sheets (MSDS) for silica sand state that "excessive inhalation of crystalline silica is a serious health concern"[18].

Silica

Silica is a compound of silicon and oxygen got either by purifying sand or reaction between silicon and oxygen, or by some other chemical reactions. Methods of sand purification includes: microbial leaching, flotation, scrub, acid leaching, magnetic separation etc. Gravimetric methods are used for silica estimation in sand sample. SiO_2 is found in nature in mainly two forms: crystalline and amorphous. It is the most abundant compound of silicon found on the earths crust and one of the most commonly found oxides. Amorphous form of silica is pure sand while quartz is an example of crystalline silica.

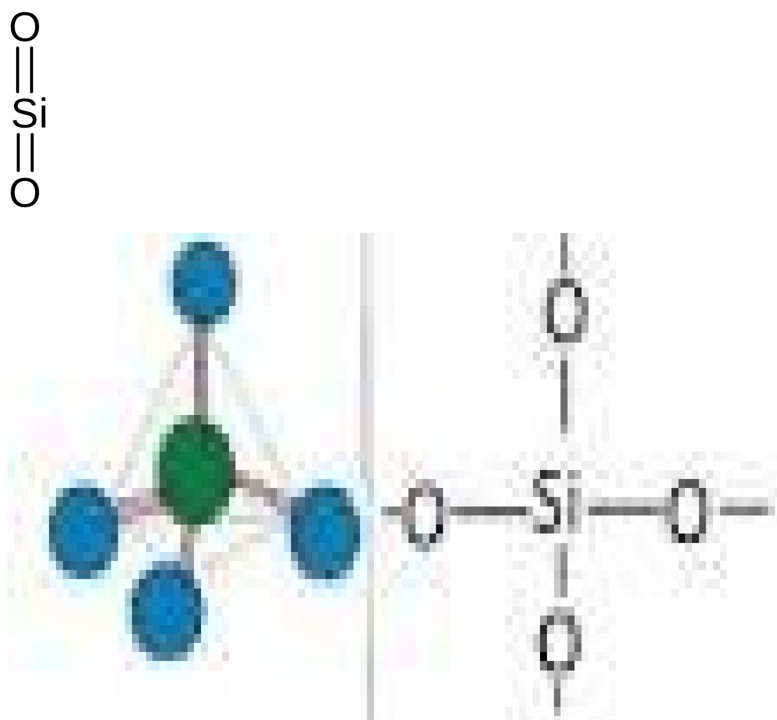

Figure 2.3: Molecular structure of silica (Source: Ref. 19)

Silica occurs in nature in more than thirteen different forms each one slightly varying from the others. The physical properties might be different but the chemical properties remain the same irrespective of their structure. Understanding of its many properties requires that we have a basic idea about the molecular structure of the oxide of silicon.

The building block of the structure of silica is the SiO_4 unit. The structure of the crystalline forms of silica is represented as continuous links of the SiO_4 unit. Figure 2.3 shows the structure of silica. Looking at the atomic model of silica (Fig. 2.3), it is obvious that the 4 oxygen atoms are located far apart from the silicon atom at the centre, with the molecule forming a tetrahedral structure.

Some facts about the molecular structure of silicon dioxide

The angle formed between each O—S—O bond is 109.5^0. However, in quartz, this angle is around 144^0.

There is uneven charge distribution between parts of the tetrahedron, with the centre being highly positive and the corners being strongly negative. This is because of the strong polarity of the Si—O bond[20].

In gaseous state, the structure of silica forms linear O=S=O molecules.

Each individual silica tetrahedron is connected with adjacent tetrahedron at the corners, forming a 3-dimensional structure.

The bridge formed by the oxygen atoms, between the silicon atoms of adjacent tetrahedrons is responsible for some of the unique properties of silica. The tetrahedral shape is responsible for the rigidity of the silica molecule. The length of the Si—O bond is 0.16nm. The molecular formula of silicon dioxide is SiO_2 while the structure shows four atoms of oxygen surrounding each silicon atom; the reason is that every individual tetrahedron shares each of its four oxygen atoms with the neighboring tetrahedron, which makes the net chemical formula to be SiO_2[20].

Physical properties

Due to the tetrahedral structure, the melting point of silica is very high. The strong Si—O bonds get broken at very high temperatures close to 1700 ^{O}C. Silicon dioxide is very hard and rigid; this is due to the strong covalent bond between silicon and oxygen. Due to the absence of free electrons within the molecular structure, silica is a very bad conductor of electricity and acts as an insulator. Silicon dioxide is insoluble in water and in all organic solvents. However, it is soluble in alkalis and hydrofluoric acid.

Table 2.1: Some Physical Properties of Crystalline and Amorphous Silica

Physical property	**Unit**	**Crystalline**	**Amorphous**

Melting point/Glass Transition Temp.	Degrees Celsius	Approx. 1700	Approx. 1700
Density	gcm^{-3}	2.6	2.2
Refractive index	-	1.46	1.46
Resistivity	Ohm-cm	10^{12}-10^{16}	Greater than 10^{18}
Thermal conductivity	$Wm^{-1}K$	1.3	1.4
Poisson's ratio	-	0.17	0.165
Coefficient of thermal expansion	K^{-1}	7.64×10^{-7}	5.4×10^{-7}

Table 2.2: Chemical Properties

Silicon dioxide reacts with very few substances. Here are some of the common reactions of silicon dioxide and their products[21].

Reacting substance.	**Reaction condition**	**Product formed**	**Chemical equation**
Strong alkalis such as NaOH and KOH	Crystalline SiO_2 dissolves very slowly in hot alkaline solutions, whereas its amorphous form reacts with alkalis at room temp.	Silicate of potassium or sodium.	$SiO_2 + 2KOH \longrightarrow K_2SiO_3 + H_2O$. $SiO_2 + 2NaOH \longrightarrow Na_2SiO_3 + H_2O$.
Hydrofluoric acid (HF)	Quartz does not react with other acids but dissolves in HF, the reaction takes place at room temp	Hydrofluorosilicic acid (H_2SiF_6)	$SiO_2 + 6HF \longrightarrow H_2SiF_6 + 2H_2O$
Sodium carbonate (Na_2CO_3) and Potassiumcarbonat	Silica reacts with molten carbonates of sodium and potassium	Silicates of sodium and potassium (K_2SiO_3 &	$SiO_2 + K_2CO_3 \longrightarrow K_2SiO_3 + CO_2$ $SiO_2 + Na_2CO_3 \longrightarrow$