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Alpha, Beta and Gamma Alumina as a catalyst -A Review

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Abstract

Alpha (α), Beta (β) and gamma (γ) are the different phases of Alumina. The α - Alumina is also known as Nano alumina and is white puffy powder. The specific surface area is low, resistant to high temperature and inert, but it does not belong to activated alumina, and it has almost no catalytic activity. β - Alumina is hexagonal, with lamellar structure and the unit cell contains two alumina spinel based block. γ -Alumina is nano alumina and has high purity and excellent dispersion and high specific surface, with resistance to high temperature and inert, high activity. Porous, hence it is a kind of activated alumina and used as catalyst support and adsorbent.

Aim is to use γ -alumina catalyst for Alkylation of phenol for Meta cresol selectivity. Literature survey indicates that its use has been studied for selectivity and yield of o cresol, 2,6 xylenol but not for meta selectivity for the reaction-Alkylation of phenol.

Challenge is to develop Gamma Alumina/Modified Gamma alumina catalyst for the study of selectivity of Meta cresol in Alkylation of phenol.

Keywords: Alpha (α), beta (β), gamma (γ) Alumina catalyst, Alkylation, Selectivity.

Introduction

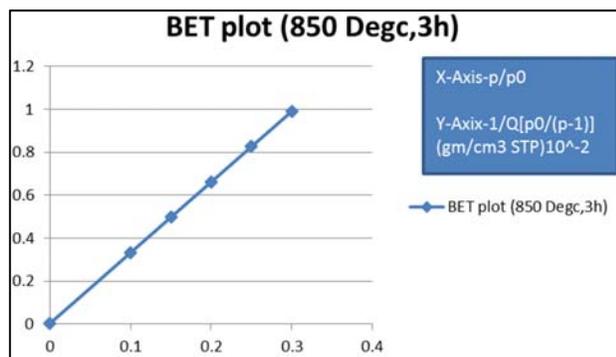
Alumina is widely used as basic material of catalytic support because of its high chemical inertness, strength and hardness. γ - Alumina possesses excellent surface area owing to the small particle size, which results in high activity of the surface for a catalyst support [1]. Mesoporous alumina has excellent properties such as highly uniform channels, large surface area and narrow pore size distribution. It has been widely used as adsorbents, catalysts support, and other ceramic applications [2]. Alumina is an important material that can be prepared from bauxite or kaolin in several different phases. The most stable form of alumina is α -alumina, which is employed as a ceramic material. Other phases of alumina, known as transitional alumina are widely used as catalysts, catalytic supports or adsorbents. Among the transitional alumina, gamma-alumina is the most employed one for applications in catalysis and adsorption, because of its high surface area and good porosity parameters [3,4].

Catalyst support is the material, usually a solid with high surface area to which catalyst is affixed. Typical supports include various kinds of carbon, alumina and silica. The reactivity of heterogeneous catalysts and nano-material-based catalysts occurs at the surface atoms. Consequently great efforts are made to maximize the surface area of a catalyst by distributing it over the support. Gamma-Alumina is a good material for catalyst support and its surface properties is of great importance. In this study the gamma-alumina (γ -Al₂O₃) synthesized used as catalyst support for zeolite catalyst was obtained by calcinations of ammonium alum an intermediate product prepared from kaolin which was sourced from Kankara, Katsina, Nigeria. The scholar has described the method and the parameters like calcinations temperature and corresponding surface area of 825 degc and 120 Sq m/gm similarly 850 Deg C of 140sq.m/gm respectively. BET technique was used for determining the properties and found XRD patter obtained has confirmed with the standard γ -Alumina corresponding to 825 and 875 DegC. The study shows the effect of calcinations temperature on the average pore diameter (size) and pore volume of the gamma-alumina developed. The optimum range of the average pore size was obtained between 840oC and 850oC. Beyond 850oC the pore size began to decrease, this may be attributed to the collapse of larger pore particle to smaller pore particle possessing larger surface area.

Brunauer–Emmett–Teller (BET) plots for various temperatures have been noted in the referred literature. At 850Degc with 3 hrs soaking time has resulted to optimum values of the average pore size and pore volume and for the said condition of 850Deg C for 3 hrs soaking time, line

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equation for the graph stated in referred literature is $Y=3.29X+0.003$. Based on the equation plot between $1/Q[p_0/(p_0-p)]$ on Y-axis and p/p_0 is on X-axis has been give below for said optimum surface area.



Thermal effect on surface properties of γ -Alumina synthesized from Kankara Kaoline (At 850 Deg C and 3 h)

Similarly composition of commercial γ -Alumina and synthesized γ -alumina data based on the literature is stated below.

Oxides	commercial	Synthesized
Al ₂ O ₃	89.80	85.02
SO ₃	2.54	4.76
SiO ₂	0.03	Not Detectable
Fe ₂ O ₃	0.17	2.67
LOI	5.21	5.16
Other Oxides	2.25	2.19

Thus based on the data gamma-alumina Produced from Kankara kaolin was similar to the commercial γ -alumina and comparative data is as stated above is based on the referred literature [5].

Scholar A. Eliassi had prepared as a precursor by strict control of pH and reaction temperature by using Bohemite (Aluminum oxy-hydroxide) and reported about preparation of nano-sized gamma alumina having high specific surface area and high yield resulting from the reaction between aluminum nitrate and sodium carbonate, without using any surfactant. Reported leaf flower shaped gamma alumina of 91% yield, having specific surface area of 413 m²/g and average pore volume 1.624 cm³/g. An average size of 38 micron of spherical particles contained flower leaf shaped γ -Alumina was observed from the study by the researcher. Gamma alumina is a long known important catalyst which has been used in various processes. It can be prepared by different methods. Morphology of synthetic gamma alumina can be changed by varying some of the reaction parameters like temperature, pressure, reaction time, thermal decomposition routes and methods of preparation, precursors, reactants and so on. The catalytic properties of gamma alumina depend on its physical properties such as surface acidity, porosity, and pore size of particles [6].

M. Zamora has reported A statistical-mechanic study of the surface dehydration of γ -alumina ma The surface monolayer is treated as a monomer-asymmetrical dimer system on a square lattice, thus only nearest neighbors interact. The scholar has studied evolution of a wide set of surface ionic groups and explains effectively the experimental data of thermo-gravimetric analysis, infrared spectra, and mobility of surface ions at $T > 600$ °C. The contributions to the activation

energy of the different surface interactions have been estimated, giving $e_{\text{O-O}} = 2$ kcal/mol. (oxide-oxide interaction), $e_{\text{HO}} = 1$ kcal/mol (hydroxyl-oxide interaction), and $e_{\text{H-O}} = 0$ kcal/mol (hydroxyl-hydroxyl interaction). The adsorbed water molecule energy is a surface coverage function and falls between -26 and -89 kcal/mol, within the expected range [7].

The reference reports that Supported mesoporous g-Al₂O₃ membranes deteriorate and blister in steam-containing environments at high temperatures. The factor has led Scholar for development of a new type of supported g-Al₂O₃ membrane having significantly improved stability under hostile conditions and two measures were considered for achieving the results 1-- Stabilization of g-Al₂O₃ itself by an addition of 6 mol% La₂O₃ to suppress pore growth of the mesoporous structure. 2-Improvement in adherence of the g-Al₂O₃ membrane to the a-Al₂O₃ support by appliace of phosphate bonding between the membrane layer and the support, by means of an Al (H₂PO₄)₃ precursor solution. The reference has reported newly developed membranes could be operated for 100 h at 600°C in H₂O/CH₄ 5 3/1 (by volume) at 2.5 MPa total pressure with no de-lamination or cracking in the membrane-support interface and with no significant pore growth in the g-Al₂O₃ membrane [8]. Masami Inoue and Saburo Enomoto has studied on meta alkylation on alumina catalysts and results shows that meta cresol up to 38.3% and total conversion upto 82.8% using Al₂O₃ catalyst [9].

Based on the reference review literature , various scholars have used various catalyst like Vanadium chromium mixed oxide, H-ZSMS Zeolite, TiO₂, SiO₂,MgO Supported V₂O₅, AlPO, SIPO Molecular sieve, Sulphates supported γ -Alumina, Cu-Al-Hydrotalcite, CeO₂-MgO, various metal oxides, γ -Alumina and modified γ -Alumina catalyst, specific molar gel sieve and resins for Alkyaltion of Phenol. Various scholars have studied alkylation of phenol for various parameters such as selectivity of the catalyst, effect of temperature, molar ratio, feed flow rates on selectivity of formation of ortho cresol, 2, 6 DMP, anisole resulting in various observation resulting to higher yield in ortho, and 2, 6 DMP. Though higher selectivity has not been experiential for meta cresol by direct phenol alkylation and not much center of attention has been given to formation of meta cresol by phenol alkylation [10].

The Scholar has studied alkylation reactions over ZnFeAlO₄ in the temperature range 275-425Deg C. It indicates that rise in temperature from 250 to 350oC, phenol conversion increased from 30 to 96% and reported a maximum at 350oC and also noted that Carbon deposition reduces the activity and conversion by further increase in temperature Another significant finding was the increase in yield of 2, 6-xyleneol from 15 to 70.9% with a high selectivity of 73.5% at 350oC as results of high activation energy needed for formation of 2, 6-xyleneol. Literature indicates carbon deposition on the surface resulting into suppression in the rate of consecutive methylation leading to decreased yield and selectivity of 2,6-xyleneol by increasing further increase in temperature above 350 Deg C. [11].

Mesoporous Al-MCM-41 molecular sieve materials with three different SiO₂/Al₂O₃ ratios were used as catalysts for Alkylation of phenol with methanol. Reaction parameters like temperature, feed flow rate, the reactant mole ratio and the catalyst SiO₂/Al₂O₃ ratio have considerable influence on the formation of products. Study indicates lower temperature, lower molar ration of methanol and lower acidity of catalyst enhances ortho-cresol with optimum WHSV of 1.78h⁻¹ while

C-Alkylation is favored by higher acidity and O-Alkylation is favored by lower acidity of the catalyst. Higher temperature, high contact time, high mole ratio of methanol in the feed and higher acid strength of the catalyst favors double alkylated products. Various oxide catalyst for alkylation of phenol with methanol for conversion to O-cresol is an established reaction. The study in referred literature shows that Al-MCM-41 be able to likewise bring about high selectivity for *o*-cresol formation. The Alkylation of phenol with methanol. *O*-, *p*-directing, there should be very little production of *m*-cresol, while the *o*- and *p*-cresols should have equal yield. The referred case, though, the selectivity for *o*-cresol was much more than the *p*-cresol and *m*-cresol)^[12].

Conclusion: γ -Alumina shows catalytic activities, hence mostly various scholars have used γ -Alumina and its modified forms and studied alkylation of phenol and various other reactions. Main focus was on selectivity, conversion and yield of O-cresol, 2, 6 DMP and effect of various parameters like molar ratio, temperature, and flow for the said reaction. However selectivity of meta cresol has not been paying attention so far. My research topic is selectivity of meta cresol in Alkylation of phenol and challenge is to develop γ -Alumina or modified γ -Alumina catalyst for selectivity of meta cresol as part of my research work.

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