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NICKEL ALUMINATE ($NiAl_2O_4$): AN EFFICIENT CATALYST FOR ORGANIC TRANSFORMATIONS

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ABSTRACT

Nano-sized crystal materials of $NiAl_2O_4$ metallic doped catalyst has beenproductively created by sol-gel combustion manner with the proper proportions of glycine supported nickel nitrate, alumnium nitrate and heated under the highest temperature on 900ºC performed into the muffle furnace. The structural, morphological and spectral properties have been examined by using FT-IR, EDS and FESEM study exposed the formation of crystalline $NiAl_2O_4$ Nano-particles. This afforded metals catalyst has been employed as catalyst in the synthesis of different substituted amine derivatives by conventional method. It was found that the highest yield acquired in the synthesis of the N-substituted formamide derivatives by the application of nickel aluminate nano-catalyst.

KEYWORDS: *Sol-gel-combustion, nickel aluminate catalyst, Substituted formamides.*

INTRODUCTION

Oxide spinels are a large category of compounds of mixed-metal oxides crystallizing into AB_2O_4 kind structure. The nickel aluminate spinel has received attention as a catalyst solid support due to its stability, substantial resistance to acids and alkalis and high melting point [1]. The $NiAl_2O_4$nano-material possesses a unique structure consisting of grains, grain limits, surfaces and pores, creating it appropriate to be used as catalyst support once its microstructures are measured [2]. In recent times, the development of $NiAl_2O_4$ for advanced applications, particularly as a solid support for metal catalysts, has been dispensed. The synthesis of $NiAl_2O_4$ to be used as nickel catalyst support for the hydro-dechlorogenation of the trichlorobenzene within the gas phase, transformation of nickel or aluminium stratified double hydroxides to nickel or corundum and nickel or nickel aluminate composites that have found utility as methylated catalysts within the treatment of carbon monoxide gas, irritating gases, replacement process material based on the addition of the new binder nickel aluminate and applied it to chemical process combustion, preparation conditions for nickel aluminum hydroxide gels and calcination temperatures on the ultimate structure of the nickel aluminate [3-6]. It is found in various natural products and also one of the most productive moieties in the modern chemical, agricultural, medicinal and pharmaceutical molecules. Formamides are so valuable compound in pharmaceutical industry [7-9]. In pharmaceutical's nitrogen containing compound are require in high demand and formamide are good to protect the nitrogen in amines. It is frequently recognized that the nano-particles with well-ordered size and conformation have been shown the fundamental and scientific importance. The fabrication method decides not only the products appearances such as size and shape, but also their physical properties. Aluminates are commonly manufactured by the ceramic technique which involves high-temperature solid state reactions lined by the oxide constituents [10-13].One of the important route to prepare aluminates is sol-gel combustion method and here the researchers has been prepared glycine assisted $NiAl_2O_4$ metal catalyst and tested their catalytic properties in the conversion of substituted amines in conventional heating synthesis.

Synthesis of $NiAl_2O_4$ Spinel System:

For the synthesis of nickel aluminate ($NiAl_2O_4$) spinel frameworks commercially bought synthetic compounds were analytical grade from Merck, India and were utilized without further purification. Aluminum nitrate, Nickel nitrate and Glycine were utilized as the fuel. The samples were set up with the expansion of Ni^{++} of molar proportions. The schematic technique for the readiness of nickel aluminate ($NiAl_2O_4$) spinel framework combined by sol-gel combustion strategy appeared by the flow diagram-1;

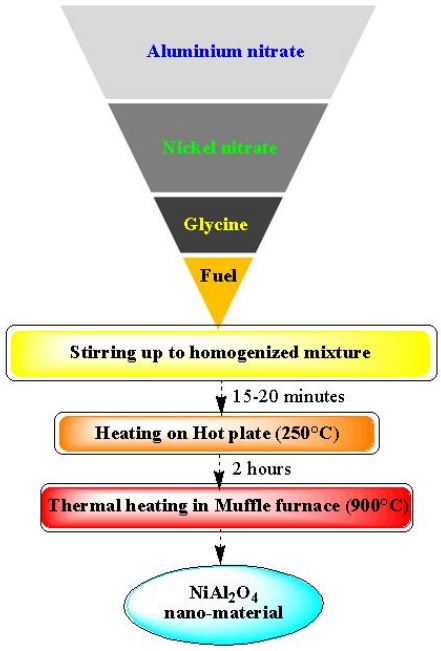


Diagram-1: Preparation flow diagram of $NiAl_2O_4$ sample

Experimental procedure for the synthesis of $NiAl_2O_4$ spinel system:

The nickel aluminate ($NiAl_2O_4$) spinel framework was blended by sol-gel combustion strategy. The technique includes wet chemical blending of the calculated proportionof 4.567g of nickel nitrate and 18.75g of aluminum nitrate and 15g glycine were gradually blended with steady mixing till the homogeneous blend with the formation of gel. The subsequent gel was heated on hot plate at 250ºC temperature for 15-20 minutes till the development of blackish char. At that point the char was collected in to the vessel and heated up to the 900ºC for 2 hours in the mufflefurnace which formsgreenish-blue colourednano-particles. These nano-particles were described by the succeeding measures for instance of the stoichiometric molar proportion of the nickel nitrate, aluminum nitrate [14].

Characterization of $NiAl_2O_4$ Spinel System:

The structural characterization of spinel $NiAl_2O_4$ sample was performed using a Perkin Elmer FT-IR spectrometertheanalysis of surface functional groups. The surface morphology of the samples was achieved at desired magnification with a Joel JSM 6360 field emission scanning electron microscope (FESEM) equipped with energy dispersive X-ray (EDS) for elemental composition analysis,reactions were monitored by GCMS, 400 MHzBruker NMR.

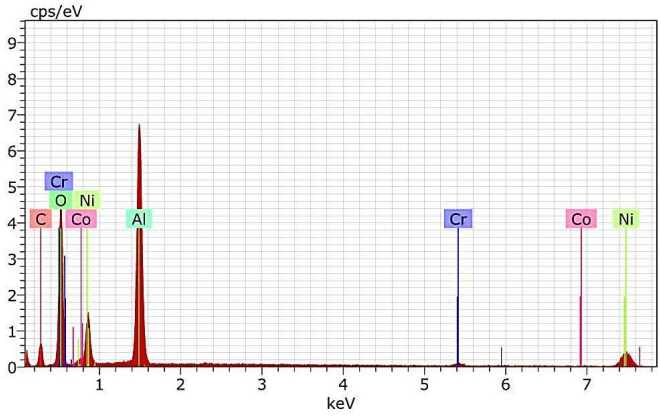
FT-IR of $NiAl_2O_4$ Spinel System:

The FT-IR spectra of spinel $NiAl_2O_4$ nanoparticles formedaninfluential and extensive absorption band detected at around in the region 3448 cm^{-1} which may be fixed to the vibrations of twofold compound

molecules. A band observed at around 1629 cm^{-1} is present in total configurations, which might be appointed to the H–O–H bending vibration. FTIR spectrum indicatesthe characteristics peaks spinal segment at about 715-508 cm^{-1} that ensures the cubical spinel structure. The detected peak at 508 cm^{-1} was associated with broadening vibration mode of Al–O for the octahedral coordinated Al^{3+} ions. Overall compositions of $NiAl_2O_4$ sample, the metal-oxygen (M–O) stretching frequencies are reportable within the range 715cm^{-1} to 508 cm^{-1}, connected with the vibrations of Al–O and Ni–O–Al bonds.

Energy-Dispersive X-Ray Spectroscopy analysis:

The chemical compositions of the catalysts determined from the EDS information have been very just like those calculated through making use of the simplest criterion that needs to be fulfilled for you to shape a perovskite-kind shape that is the ionic radii necessity introduced by way of Goldschmidt [15], consequently referred to as tolerance element defined by equation. The common theoretical composition (EDS) has additionally been calculated from the percentage of nickel and vanadium cations inside the B-sites of the perovskite, which turned into varied between x=0 for $Ni_xAl_2O_4$ and x=zero there may be excellent arrangement between the experimental and theoretical (EDS) perovskitecompositions for $NiAl_2O_4$, while the slight distinction in elemental composition is probably because of a difference in stoichiometry with regard to oxygen. EDS analysis confirmed that the homogeneity of the catalyst after the test become just like that before the patterned for x=zero, localized parts of better nickel concentrations are designed. It exhibited Ni, Al and O peaks and indicated the presence of $NiAl_2O_4$phase. The peaks at 0.5, 0.8 and 1.5 keV in the EDS spectra were due to the oxygen, nickel and aluminiumelement present in the sample before recording FESEM.



Spectra-1:EDS analysis of$NiAl_2O_4$ sample

Therefore the elemental analysis of the sample was carried out by using energy dispersive X-ray (EDS) resulting the fractions of elements in the K-series are found the weight of Ni (0.98%), Al (1.28%) and O (4.25) correspondingly. Thus it is clearly displays that the nano-crystalline $NiAl_2O_4$comprises only Ni, Al and O without any impurity.

Field Emission Scanning Electron Microscope (FESM) analysis:

The Field Emission Scanning Electron Microscope analysis of the $NiAl_2O_4$ synthesized by sol-gel combustion technique, the $NiAl_2O_4$ sample had a totally distinctive structure and surface morphology. FESM micrograph of the $NiAl_2O_4$ sample is homogenized and well defined spinel particles of nano-metric in size were proven by FESEM images by the different magnification of a singular$NiAl_2O_4$ sample. The particle morphology is kind of uniform for each sample suggesting that this technique of synthesis yields a consistent material with uniform particle sizes. The scale and particles were measured for as prepared and $NiAl_2O_4$ sample severally by the different magnification for different sizes starting from from 50000 magnifications

with 15 kV WD of 4.9 mm spot 3 under the pressure of 1.66e-4 Pa in the SE mode for the particle size 2 µm as shown in the fig-1.

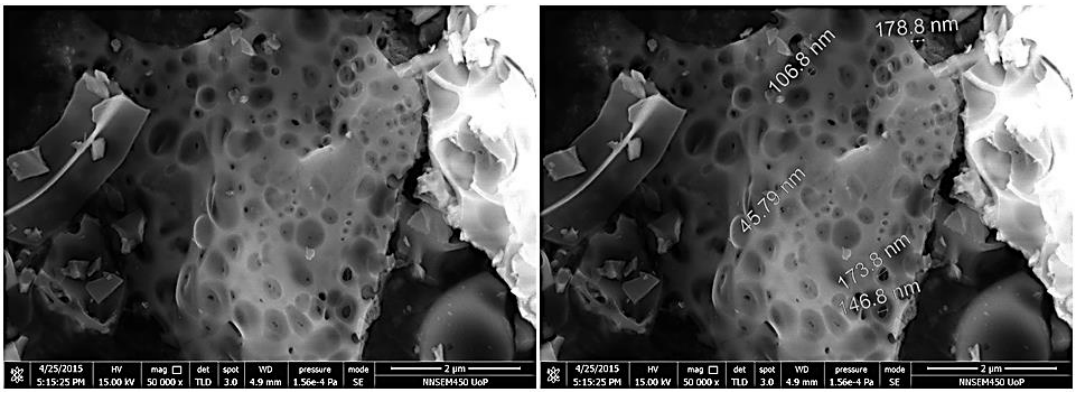


Fig-1: FESM of 2µm magnified article size of $NiAl_2O_4$ sample

Thus it was found that, the most significant particle size distribution was the specificrange that was measuredsomewhatsuperlativeappearances for the mixed metal aluminate spinel systems.

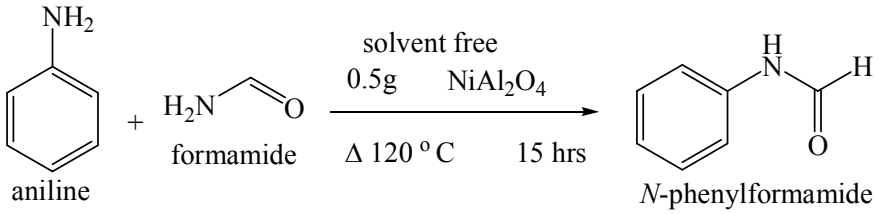
Catalytic study of $NiAl_2O_4$nanomaterial:

The applications of the developed nickel aluminate ($NiAl_2O_4$) nano-material as a catalyst for the N-formylation of amines to synthesize the substituted formamideswere accomplished. All reactions were performed by using the sealing glass tube and the yield were calculated on gas chromatography and products were analyzed by using GCMS.

Material method:

Synthesis of N-phenylformamide:

Aniline (1mmole) and formamide (1mL) was mixed with $NiAl_2O_4$ (5mg) at solvent free condition and heated under with constant stirring for 15 hours for the conversion of N-ethyl-N-phenylformamide as revealed in the **scheme-1**. The reaction was continuously monitored by GCMS. The molecular formula of the synthesized compounds is C_7H_7NO, Mol. Wt.: 121 m/z, Practical yield: 98%, FTIR (ATR): 1728, 1347, 1463, 1505 and 1634 cm^{-1}, ^1H NMR (400 MHz, DMSO d^6, δ ppm): 7.21-7.51 (m, 4H, Ar-H), 8.6 (s, 1H), obtained yield is 86%.

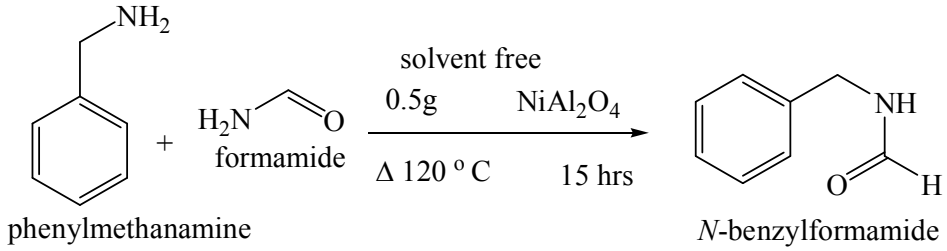


Scheme-1: Preparation of N-phenylformamides by $NiAl_2O_4$catalyst

Synthesis of N-ethyl-N-phenylformamide:

N-ethylbenzamine (1mmole) and formamide (1mL) was mixed with $NiAl_2O_4$ (5mg) at solvent free state and heated under with continuous stirring for 15 hours for the conversion of N-ethyl-N-phenylformamide as shown in the **scheme-2**. The reaction was constantly monitored by GCMS. The molecular formula of the prepared compounds is $C_9H_{11}NO$, Mol. Wt.: 149 m/z, Practical yield: 98%, FTIR (ATR): 1719, 1297, 1451, 1518 and 1614 cm^{-1}, ^1H NMR (400 MHz, DMSO d^6, δ ppm): 7.19-7.46 (m, 4H, Ar-H), 1.0 (t, 3H), 8.1 (s,

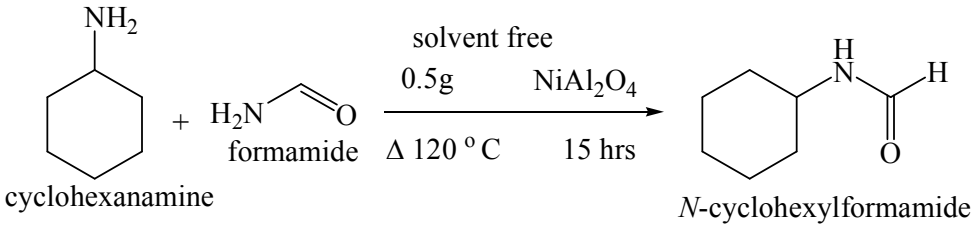
1H), 71% yield obtained.



Scheme-2: Preparation of N-benzylformamides by $NiAl_2O_4$ catalyst

Synthesis of N-cyclohexylformamide:

Cyclohexamine (1mmole) and formamide (1mL) was mixed with $NiAl_2O_4$ (5mg) at solvent free condition and heated under with constant stirring for 15 hours for the conversion of N-cyclohexylformamide as presented in the **scheme-3**. The reaction was constantly monitored by GCMS. The molecular formula of produced compounds is $C_7H_{13}NO$, Mol. Wt.: 127 m/z, Practical yield: 95%, FTIR (ATR): 1719, 1297 and 1614 cm^{-1}, ^1H NMR (400 MHz, DMSO d^6, δ ppm): 7.19-7.46 (m, 4H, Ar-H), 1.0 (t, 3H), 8.0 (s, 1H), 1.60 (m, 10H), 8.55 (s, 1H, -NH), yield 85%.



Scheme-3: Preparation of N-cyclohexylformamides by $NiAl_2O_4$ catalyst

RESULT AND DISCUSSION:

It was revealed that with increase in the quantity of catalyst the product yield of the sample reaction increases. The reason for increasing catalyst is mainly due to increase in active sites with increase in the amount of catalyst and increasing the practical yield. Hence it has been used the amount of catalyst as 5mg for the rest of the reactions. To consider the extent of the response researchers can be utilized different subordinates of amines to research two segment responses under streamlined condition and the time of the reactios with higher temperatures.

It was found that different amine derivatives could be utilized resulting great percentage yield by using newly prepared $NiAl_2O_4$nano-catalyst in the synthesis of amine derivatives with formamide.

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