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Physicochemical properties of doping Nickel –Cobalt oxides catalysts supported on SiO_2 and its catalytic activity

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The physicochemical and catalytic properties of low-cost metal mixed oxide catalysts have been researched and characterized. To explore catalysts, various characterization techniques such as BET and X-ray diffraction (XRD) have been utilized. Three distinct catalysts, C1(NiO-Co_3O_4/Silica), C2(NiO- Co_3O_4-ZnO/ Silica), and C3(NiO- Co_3O_4-BaO/ Silica), are synthesized with 20 wt% mixed oxide (NiO- Co_3O_4) supported on silica and doped with zinc/barium oxide, and then dried at 110°C overnight and calcined at 350^{o}C All three catalysts have been tested in an ethyl acetate saponification reaction, and the conversion of reactants is calculated. In comparison to the other catalysts, C2 (NiO-Co_3O_4-ZnO/ Silica), which is a combination of NiO-Co_3O_4/SiO_2 doped with zinc oxide, show good catalytic activity. In terms of catalyst doping, the addition of zinc oxide to the Silica supported original composition boosted the catalytic activity for the saponification reaction compared to barium oxide and without doped.

Keywords: Barium oxide, Ethyl acetate, Mixed oxides, Saponification, Zinc oxide

Modern catalyst manufacturing businesses face a difficulty in maintaining price competitiveness in catalyst preparation. There are various less expensive metals that have good catalytic activity, therefore there is a lot of room to produce a less expensive catalyst for today's needs. The major criteria for selecting a catalyst for the process are selectivity, yield, and conversion ratio. There is a lot of study going on right now to develop theories and models to beat platinum and precious metals. The most difficult task is to obtain high activity and selectivity in order to meet industrial demands. A catalyst can be made in a variety of ways, and the method used for a specific catalyst is determined by what the researcher wants in the final product. In short, a number of preparation options for a specific base material might be considered. Metal oxide catalysts' catalytic activity and selectivity could be altered by a modest quantity of doping of a foreign oxide[1-3]. Because of their mutual interaction, combining transition metal oxides result in the development of complex spinel or perovskite structures[4,5]. Mixed oxide catalysts have been demonstrated to have better catalytic activity than individual oxide catalysts in numerous studies[6,7]. Silica is one of the most convenient supports, and it is utilized in the synthesis of a wide range of catalysts and in a wide range of processes, particularly oxidation-reduction reactions[8,9]. The catalytic activity of Silica supported catalysts decreases as the application/use time increases. This is because as the catalyst is employed for longer periods of time, more metal Silica forms occur, resulting in reduced catalytic activity compared to metal oxides supported by Silica[10,11]. The interaction between Silica and metal oxides produces metal Silicate, and the rate and quantity of formation are greatly dependent on the nature of the transition metal element. In their findings, the authors[11] established that Silicate is formed in the following order: Cu>Co>Ni>Fe. Due to their optical and magnetically unique properties, NiO and Co_3O_4 with optical band gaps of 3.6-4e V (Eg=3.6-4 e.v) and 1.2 e V (Eg= 1.2 e V) act as P-type semiconductors with a variety of applications such as catalysts, sensors, optical devices, electrochemical supper capacitor transparent P-type semiconducting layer, and antiferromagnetic film, among others[12-16]. ZnO is a semiconductor with a high exciton binding energy of roughly 60meV, which makes it ideal for lasing. This ability of ZnO as a semiconductor piqued the interest of many researchers[17-19]. Polariton/exciton interaction is conceivable even at room temperature due of ZnO's high exciton binding energy[20]. Cu sintering is slowed when zinc oxide is added as a promoter to cobalt oxide. When it comes to transition metal doped barium tartrate crystals or others, contaminants in the growth media have a significant impact on crystallization processes. In the literature, there is a scarcity of information about their growth, characterization, and qualities[21,22] investigated the development, characterisation, and characteristics of cobalt-doped barium tartrate crystals, which were then employed in a variety of applications. Research[23-25] shows how doping modifies the characteristics of materials. Although studying the effect of dopants on crystal development and characterization is difficult, the research of doped crystal growth and characterization has received a lot of interest in recent years[26]. Chemical affinity cations, product solubility, diffusivity, dehydration enthalpy, and ionic radii, are among other parameters that influence crystal formation and characterization[27]. Many factors influence the structural features of produced catalysts, including the choice of the three major catalyst constituents: support, active component (metal, oxides), and promoters[28]. The goal of this study was to use impregnation methods to make acceptable catalysts from available metals such as a blend of nickel and cobalt compounds supported on Silica. It will be investigated the influence of ZnO or BaO doping on the manufactured mixed oxide supported on Silica. Characterization procedures included BET Surface Area and X-ray diffraction (XRD). For the saponification reaction, the catalytic activity of the produced catalysts C1, C2, and C3 are also determined.

Experimental Section

Materials

Silica oxide, nickel nitrate, cobalt nitrate, barium nitrate, and zinc nitrate, as well as ethyl acetate and sodium hydroxide pellets, were acquired from LOBA Chemie, Honeywell Riedel-de Haan®, and PanReac AppliChem, a laboratory reagents and fine chemicals provider. All chemicals used in the preparation of catalysts are utilized without any pre-purification.

Preparation of catalysts

The desired catalysts were prepared using the impregnation technique. A known mixture of nickel and cobalt nitrates were dissolved in a known amount of distilled water and impregnated into fine silica powder. It was ensured that the mixture was well mixed and swirled constantly at a temperature of 50°C for a sufficient amount of time. As doping materials, zinc or barium nitrate were added to the well-mixed solution. The new solution was left for a sufficient amount of time, and then dried overnight at 110°C in a dryer. After drying, the composite materials were crushed into powder and fired in a furnace for four hours at 350 degrees Celsius. The quantity of each component stated as wt. 10% NiO and wt. 10% Co_3O_4.

Catalytic reaction experiment

The catalytic activity of various produced catalysts was determined using a liquid phase saponification process between sodium hydroxide and ethyl acetate. In a 100ml glass reactor, all reactions were carried out at ambient temperature. A continuous magnetic stirrer was installed in the glass reactor. To determine the reaction progress, the conductivity of reacting components was measured. The conductivity was measured every two minutes until the steady state was reached.

Characterization

The specific surface areas (S_{BET})of thevariously synthesized catalysts were determined from N_2 adsorption isotherms measured at 77 K using NOVA 4200e apparatus. X-ray powder diffraction patterns of various investigated samples calcined in air at 350^oC were carried out using a Panalytical diffractometer (Xpert Pro, Hollanda) . The patterns were run with CuKα with secondly monochromatic (λ=1.5406 A0) at 450kV 40 mA).

Results and Discussion

Synthesis and Characterization

The goal of this project is to synthesize catalysts from abundant metals that are inexpensive to get, as well as to investigate their properties and reaction activity. Nickel Nitrate (Ni $(NO_3)_2$), Cobalt Nitrate (Co $(NO_3)_2$), Zinc Nitrate (Zn $(NO_3)_2$), and Barium Nitrate (Ba $(NO_3)_2$) were employed for this. The first catalyst is NiO- Co_3O_4 supported Silica, the second is NiO- Co_3O_4supported Silica doped with zinc nitrate, and the third is NiO- Co_3O_4 supported Silica doped with barium nitrate. Catalysts were prepared as described in section 2.2, with all processes from weight through calcination carried out meticulously. Catalysts were prepared and then characterized in a very scientific manner. For characterisation, BET Surface Area and X-ray Diffraction (XRD) were utilized. To compare the synthesized catalysts, the prepared catalysts C1, C2, and C3 were characterized, each characteristic is described in greater depth below, one by one.

BET surface area

From N_2 adsorption isotherms measured at 77 K using the NOVA 4200e equipment, the specific surface areas (SBET) of the three produced catalysts C1, C2, C3, and pure were determined. Before performing BET measurements, all samples were degassed at 300°C for 3 h under vacuum. Table 1 shows the results of the BET study for all produced catalysts. Figure 1 shows a comparison graph of adsorbed per gram of weight of each catalyst at reduced pressure. Characterization by BET Table 1 shows the average pore diameter (A), pore volume (cm^2/g), and BET surface area (m^2/g) of the catalysts C1, C2, and C3 as well as the average pore diameter (A), pore volume (cm^2/g), and BET surface area (m^2/g).

The results show that treated silica with a mixture of nickel and cobalt oxide has a specific surface area of $69.23 m^2/g$, indicating that the coexistence of Co_3O_4 and NiO oxide on the Silica. The SBET of the zinc nitrate and barium nitrate doped catalysts C2 and C3 are 89.45 m^2/g and 59.96 m^2/g, respectively, when compared to the 69.23 m^2/g surface area of catalyst C1.

These results could be attributable to the formation of novel phases in C1, C2, and C3 based on the components present in each catalyst, such as cobalt/nickel silicate, zinc silicate, and barium silicate. It is reasonable to suppose that the Co_3O_4 and NiO phases are evenly distributed on the support and cause only minor changes in porosities. The results show that due to a change in the crystal structure, treated silica with a mixture of mixed oxides doped with zinc oxide has a higher surface area than treated silica with a mixture of mixed oxides doped with barium oxide.

X-ray diffraction (XRD)

The provider supplied a certain mass of finely powdered silica, which was impregnated with a solution containing a known amount of nickel and cobalt nitrates dissolved in a known amount of distilled water. At a temperature of 50°C, the mixture was agitated for a long enough period to ensure thorough mixing. A calculated amount of zinc or barium nitrate was added as a doping agent to the aforesaid mixed solution and left for enough time for good mixing before being dried overnight at 110°C in a drier. Following the completion of the drying process, all samples were crushed to a powder and heated for 4 hours in a muffle furnace at 350°C. The components were calculated as wt10% NiO and wt. 10% Co_3O_4.

Table 1 — BET surface characteristics of the catalysts.

Sample code	Composition	Calcination temperature (deg C)	BET area m2/g	Pore volume cc/g	Average pore diameter (nm)
C1	10%NiO-10% Co_3O_4/ SiO_2	350	69.23	0.1212	0.8627
C2	10%NiO-10% Co_3O_4- 0.2% ZnO/ SiO_2	350	89.45	0.1502	0.8564
C3	10%NiO-10% Co_3O_4- 0.2% BaO/ SiO_2	350	59.96	0.1027	0.8721

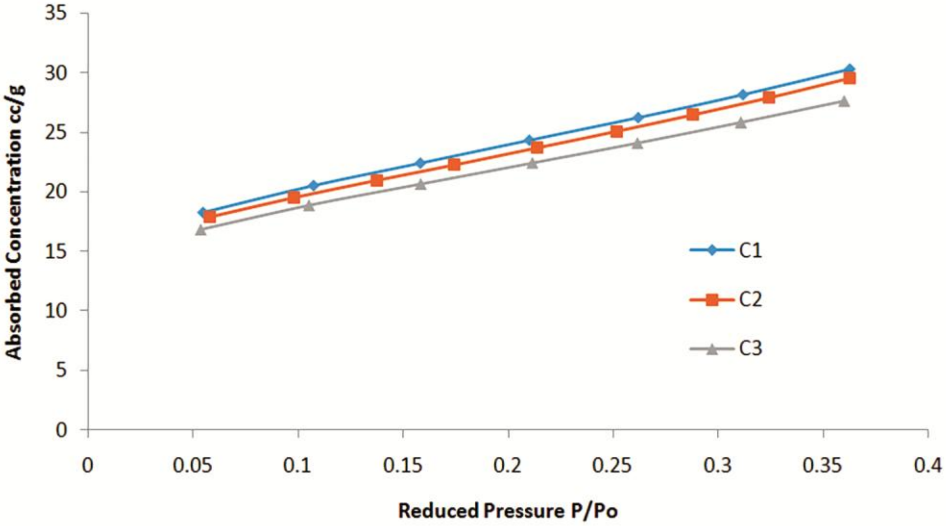

Fig. 1 — BET Adsorption isotherms of S1, C1, C2 and C3 catalysts.

The treatment of silica with a mixture of cobalt and nickel nitrates, and then doping this mixture with zinc or barium nitrates, is based on a detailed analysis of diffractograms. The degree of crystallinity of the silica phase reduced as a result of this process, which was almost proportionate to the amount of oxides supplied.

Using a Panalytical diffractometer, X-ray powder diffraction patterns of various examined substances calcined in air at 350°C were obtained (Xpert Pro, Hollanda). At 450kV 40 mA, the patterns were performed with CuK and then monochromatic (=1.5406 A°).

Synthesis of catalysts C1, C2 and C3 which were calcined at 350°C for 4 h, was carried out at room temperature. The obtained diffraction patterns were studied carefully, Figure 2 represents the diffraction pattern of all three catalysts C1, C2 and C3.

The diffraction pattern of the samples indicated the presence of cobalt oxide (Co_2O_4), that having a degree of crystalline. The strongest three peaks were, d= 1.43753 A^0, d= 1.56898 A^0 and 2.88928 A^0 matched with 01-080-1536 Fig. 2.

Determination of catalytic activity

The catalytic activity of various produced catalysts was determined using a liquid phase saponification process between sodium hydroxide and ethyl acetate. In a 100 mL glass reactor, all reactions were carried out at ambient temperature.

$NaOH+CH_3COOCH_2CH_3=CH_3COONa+C_2H_5OH$

Sodium Hydroxide+Ethyl Acetate=Sodium Acetate+ Ethyl alcohol

The saponification reaction was carried out in a batch reactor at room temperature and pressure. A considerable degree of conversion of initial reagents has occurred after reaching the steady state. The process was carried out to calculate the conversion and rate of reaction of all three catalysts, C1, C2, and C3, in order to determine their catalytic activity.

Catalyst dose optimization

To investigate the catalytic activity of catalysts, the aforementioned model process was carried out over catalysts C1, C2, and C3. The catalytic activity of various produced catalysts was determined using a liquid phase saponification process between sodium hydroxide and ethyl acetate. In a 100 mL glass reactor, all reactions were carried out at ambient temperature.

On a known weight of catalyst, 0.1M NaOH and 0.1M $CH_3COOC_2H_5$ liquid solutions were reacted. The mass of the catalysts was tuned using three distinct masses: 0.1, 0.2, and 0.3g. Each mass of catalysts was placed one by one in a 100 mL reactor volume, and conductivity data was acquired as indicated above. The influence of catalyst mass on the saponification reaction is depicted in Fig. 3. The saponification reaction demonstrated excellent conversion at ambient temperature and pressure with 0.2 g of catalyst mass.

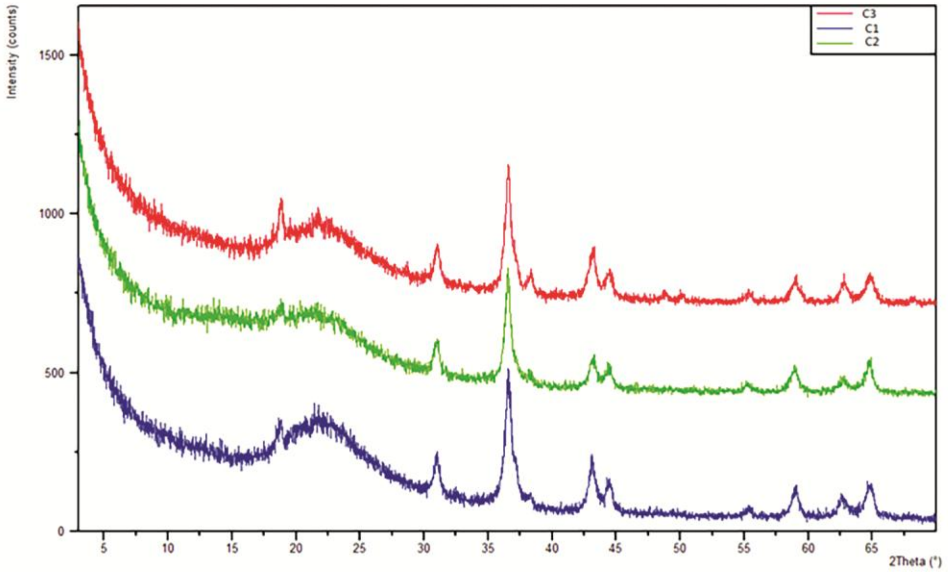

Fig. 2 — X-ray diffractgrams of Silica and mixed oxides supported Silica solid samples calcined at 350°C upto 4 h.

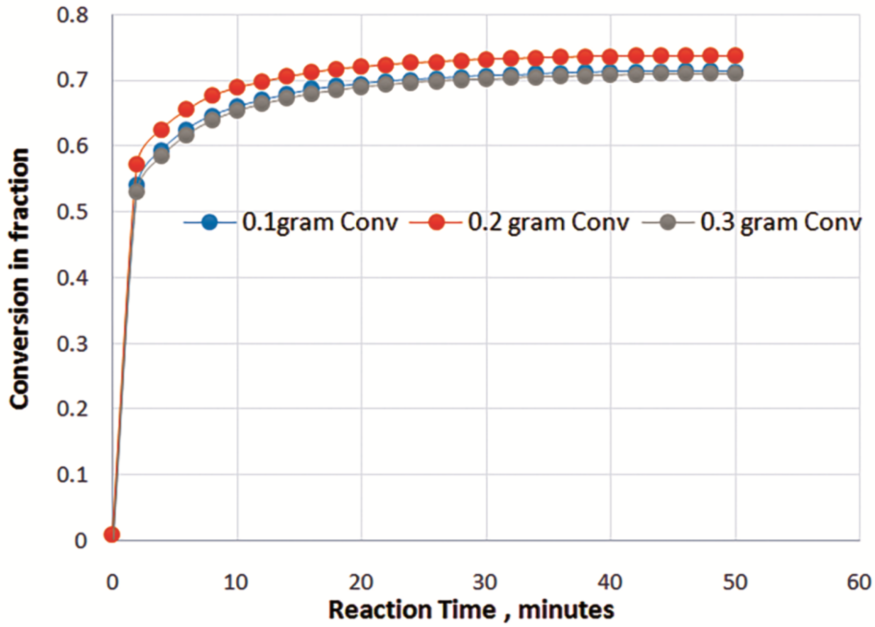

Fig 3 — Optimization of catalyst mass for saponification reaction

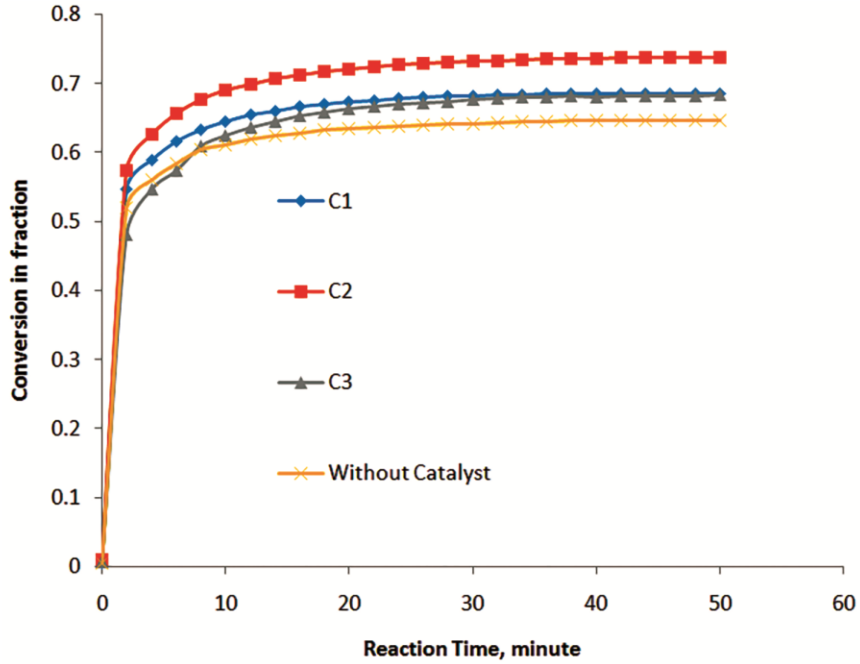

Fig 4 — Catalytic conversion results of all three catalysts and without catalyst.

Conversion and reaction rate

For a certain amount of time, the conversion and reaction rate of the saponification reaction were examined on all three catalysts C1, C2, and C3. The operating conditions (temperature, pressure, and stirrer speed) for all three catalysts were kept the same and constant.

Figure 4 shows the catalytic performance of C1, C2, and C3 with and without a catalyst. Three catalysts, C1, C2, and C3, have catalytic activity of 67 percent, 76 percent, and 70 percent, respectively, but no catalyst has catalytic activity of 67 percent. The author[29] worked on the same reaction without a catalyst and found that at reaction temperature 35°C, the greatest achievable conversion without a catalyst is 63.3 percent, which is similar to the experiment without a catalyst done in this research. When compared to other manufactured catalysts, the results demonstrate that the catalyst C2 has the best catalytic activity. C2 is a mixture of NiO-Co_3O_4/SiO_2 that has been doped with zinc nitrate, resulting in the formation of zinc Silicates in the catalyst. Compared to C1 and C2 catalyst activity, the catalytic activity of this catalyst is improved. The fact that C1 and C3 convert at the same rate indicates that adding barium as a promoter has no effect on conversion. Many studies have proven that the ethyl acetate saponification reaction is a second order reaction[30-32]. Catalysts C1, C2, and C3 have reaction rate constants of 0.1607, 0.1783, and 0.1590 L mol^{-1} min^{-1}, respectively.

Conclusion

These are some possible conclusions based on the findings and conversations.

The loading of cobalt nitrate and nickel nitrate on the Silica solid sample up to 10% NiO and 10% Co_3O_4, followed by calcinations at 350^{o}C for 4 h, results in partial dissolution of nickel and cobalt species in the Silica lattice, forming solid solutions, while the remaining portion remain as separate Co_2O_4.

The coexistence of Co_2O_4 and NiO on calcined Silica at 350^{o}C prevents both Co_3O_4 and NiO from dissolving in the Silica lattice due to a putative solid-solid interaction, resulting in NiCo3O4.

When compared to catalysts C1 and C3, the catalytic activity of catalyst C2 on the saponification reaction indicated greater conversion.

It can be concluded that the addition of zinc nitrate to the original composition C2 (nickel-cobalt oxide supported on Silica) has higher catalytic activity than barium nitrate due to the formation of the zinc Silicates phase, and thus the addition of zinc to mixed oxides system is better than barium in terms of effect of doper on mixed oxides catalyst system.

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