Catalytic Hydrogenation of Organic Polymers by Mixed Transition Metal Oxides

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Abstract:- **Plastic pollution is inviting a global environmental crisis. Plastic production and its corresponding waste generation are increasing dramatically as a result of growing populations, continued urbanization, and changes in modern lifestyle. Moreover, the problem of this extremely useful product is its long life. Converting waste plastics into liquid and gaseous products is considered a wise alternative to minimize the damage to the environment and moreover, decrease the dependence on fossil fuels. The idea of de-polymerization of plastics into other products is its conversion into monomers and subsequently into platform chemicals. In this regard, here we report the catalytic conversion of Polystyrene (a synthetic product from styrene monomer, used for packing materials) into the monomers by mixed oxide catalysts (Ni-Cu-Al and Ni-Zn-Al) of 0.25g in the presence hydrogen donor (Me-OH) solvent at high temperature (350ºC). The hydrogenation of polymers is carried out by the mixed metal oxides synthesized from the precursors of Layered Double Hydroxide (LDH). The catalysts are characterized by XRD, SEM, EDX and the quantitative study of catalytic performance of these oxides are tested by GC-MS. In XRD results, the peaks of $Ni_{0.25}Cu_{0.25}Al_{0.25}$ observes at $27.42°$, $32.70°$, $36.12°$, $37.84°$, $39.16°$, $43.50°$ $49.46°$ and $60.01°$. and the peaks of $Ni_{0.25}Zn_{0.25}Al_{0.25}$ strikes at $28.25°$, $31.84°$, $36.12°$, $38.04°$, $45.15°$ and $56.78°$. In SEM results, some round, porous and lamella structure are observed but a little difference in composition and crystallinity in both catalysts. The average calculated precipitation of Ni^{+2}, Cu^{+2}, Al^{+3} is 0.26, 0.26 and 0.46 respectively in $Ni_{0.25}Cu_{0.25}Al_{0.25}$ catalysts and the average calculated precipitation of Ni^{+2}, Zn^{+2}, Al^{+3} is 0.10, 0.36 and 0.53 respectively in $Ni_{0.25}Cu_{0.25}Al_{0.25}$ catalysts in EDX analysis of both catalysts. The fragmentation of Polystyrene to benzene ring is observed in GC-MS results of both catalysts.**

Keywords:- *Polymers, Transition Metal Oxides, Catalysts, Organic Polymers, Transition Metal.*

I. INTRODUCTION

Plastics have become a common trash and which resist decomposing biologically. The large proportion about 72% plastics is usually discarded, with the remaining being consumed or repurposed in various manners. The release of polymer major pollutants has been well recognized as a significant cause of environmental damage. The production of plastic has been increased sharply over the last 6 decades[1]. The environmental crisis has been reported after immense production. Due to the endurance of the polymers used, large amounts of abandoned side plastics are accumulated as waste in landfills and other waste disposal facilities. One of the most crucial steps that can be implemented right now to lessen these effects is recycling. The benefits of recycling include a decrease in the amount of oil used, carbon dioxide emissions, and the procedure of dispose off to waste. International collaboration much needed to reduce pollution from plastics[2]. Chemical depolymerization could be used to recycle in terms of mechanical processes. In the recycling and reuse of plastics, chemical oxidation has enormous potential since the loop can be finished by generating starting subunits of polymeric materials that can be recycled to create high-value substances. By 2050, it has been predicted that over 60% of plastic may be produced using recycled materials. The target of producing 1.2 metric ton (MT) of recyclable materials in the EU by 2025 and 3.4 MT by 2030. Millions of dollars are being invested to improve chemically recycling as well as other cutting-edge technology solutions[3]. Most polymers can be reduced by pyrolysis by burning them at high temperatures and changing phase. However, since a phase transition is required and the process is carried out at a high temperature (450-800 C), more energy is often required. The main effects of catalyst addition in pyrolysis are as follows:

(1) the pyrolysis temperature to reach a given conversion is drastically reduced; (2) more iso-alkanes and aromatics can be produced in the C_5-C_{10} range, which are highly desirable gasoline range hydrocarbons; and (3) the rate of reaction is significantly increased[4]. There is another method of supercritical water for the conversion of low-density polyethylene (LDPE). Polyethylene conversion is around 30% in the following terms: 400°C temperature, 30 MPa above pressure, and 30 minutes' reaction. The effect of supercritical water on the de-polymerization of polyethylene can be described bases on the mechanism of H abstraction and β-scission reactions. The groups of three polymer processes can be distinguished by hydrogenation: heterogeneous and homogeneous catalysis and non-catalytic method. Several oxides, which including zinc oxide, can catalyze hydrogen atom addition to double bonded alkenes that under some conditions; nonetheless, transition metals are used as hydrogenation catalysts in the great majority of scientific research and practical applications[5]. Homogeneous catalysis involves mixing the catalyst and the reactants in the same phase. Homogeneous catalysis involves reactions that happen in the gaseous state or mostly in liquid phase, however some of them also happen in the solid phase. Contrarily, the reaction occurs either in the liquid or gas phase when heterogeneous catalysis is being used, as well as the catalyst is often in solid form. Heterogeneous catalysis is the process in which reaction take places in many stages. "Stage" here indicates to be strong, gas, fluids or immiscible fluids having oil and water. By and large, the impetus is in the strong stage, and the gases or fluids to be reactants[6].The some methods for de-polymerization of plastics like Pyrolysis (Zeolite catalyst for pyrolysis, Metal oxides for pyrolysis), Ionic Liquids for de-polymerization, Hydrolysis of polymers, Biological method of de-polymerization in which the protonation of C=C double bonds or, in some instances, aromatic compounds in molecular chains opens up a world of options for modifying polymer with good resistance to oxidizing agents (O_2, O_3), heating, ionizing and Ultraviolet rays, and oil products. Physical qualities like tensile, percentage elongation, longitudinal young's modulus, shape - changing after melting, and abrasion resistance are all improved in hydrolyzed polymer composites. As a result, hydrolyzed polymers are in good quality in the petrochemical, aviation, defense and nuclear energy industries, as well as products for Polar climates and lubricating ingredients[7].

II.   MATERIALS AND METHODS

The Nickel Sulphate hexahydrate [(NiSO$_4$.(H2O)$_6$](Sigma-Aldrich, USA), Zinc Chloride anhydrous [(ZnCl$_2$)] (Sigma-Aldrich, USA), Aluminum Chloride [(AlCl$_3$)] (QReC), Copper Sulphate [(CuSO$_4$)](DS Fine Chem), Sodium Hydroxide [(NaOH] (Sigma-Aldrich, USA), Sodium Carbonate [(Na$_2$CO$_3$)](ICI Chemicals) were used for the synthesis of mixed metal oxides(MMO). These mixed metal oxides were used as catalytic agent with crushed polystyrene (C_8H_8)$_n$. For the structural measurement of MMO, Bruker AXS, D8 Advance XRD machine were used. For surface morphology, the samples were seen SEM (Hitachi S4800). For the calculation of average atomic

percentage of precipitation, EDS instrument model ASTM D6481were used. For the separation of low molar mass compounds, ABI QStar Elite model of GC-MS were used.

A. Stoichiometric Calculations of Reagents

LDH = M^{+2}/M^{+3} =2

Formula LDH=$[(M^{II})_{1-x}(M^{III})_x(OH)_2]^{x+}(A^{m-}_{x/m}) \cdot nH_2O]$

$$\frac{M_1^{+2}+M_2^{+2}}{M^{+3}} = \frac{Zn^{+2}+Zn^{+2}}{Al^{+3}} = \frac{[M_{50}^{+2}]}{[M_{0.25}^{+3}]}=2$$

CO_3^{-2} = 12+ 48 =60

OH = 16+1 = (17)2= 34

Ratios × Mass required

Ni   +   Zn   +   Al

0.25×59(Ni) 0.25 ×65.38(Zn) 0.25 ×27(Al) + 34
14.75+16.345 +6.75+7.5 +34+9 = 88.435

Total Mass of Precipitated LDH required =10g
Ni^{+2} 0.25 = $\frac{0.25 \times 10}{88.345}$ = 0.028 ×262.84 (molar mass of salt) = 7.359g

Zn^{+2}0.25 = $\frac{0.25 \times 10}{88.345}$ = 0.028 × 136.31 (molar mass of salt) = 3.82g

Al^{+3} 0.25 = $\frac{0.25 \times 10}{88.345}$ = 0.028×133.34 (molar mass of salt) = 3.72g

Cu^{+2} 0.25 = $\frac{0.25 \times 10}{88.345}$ = 0.028×159.60 (molar mass of salt) = 4.469g

CO_3^{-2} Calculation   0.25/88.345= 0.00282 ×2 = 0.00564 =5.64Meq

5.64×10 = 56.4Meq

Mass of Na_2CO_3=106×56.4 =5978.4/2 =2989×10^{-3} = 2.9g

B. Selection of pH range Synthesis of LDH Precursor

The precipitation of metal hydroxides is chiefly dependent on the solution pH. However, when divalent and trivalent cations are to be co-precipitated, the solution pH must be a good compromise between the precipitation ranges of all respective cations. Therefore, in this regard, we have followed the given precipitation diagram as suggested by[8].The pH of each cation plays a crucial role in the synthesis of Lamellar Layered Double Hydroxides (LDHs). The two step process were used for mechanism of LDH formation[9]. Firstly, hydrous oxide formation processed by LDH formation. Secondly, crystallization of LDH takes place by M^{3+} diffusion inside M^{+2}oxide or M^{+2} cation diffusion into rich phase of M^+[10-12].

C. Synthesis of Mixed Metal Oxides(MMO)

The synthesis of the LDH precursor was done manually by the method of co-precipitation at pH constant value with respective divalent and trivalent cations in molar ratio at M^{+2}/M^{+3} i.e. The preparation of solution, pH, agitation time and drying time had been kept unchanged for both kinds of layered double hydroxides (LDHs). 50mL of 0.25M solution of Nickel (II) Sulphate hexahydrate and 0.25M Zinc Chloride (replaced by Copper (II) Sulphate in the second synthesis) each were prepared and mixed well. Later, 0.25M of Aluminum Chloride was added to this solution with continuous stirring. 50mL of 2.9g of Sodium Bicarbonate was prepared as an anionic solution. The cationic solution was dropped into the anionic solution by slow dropwise addition from the burette while maintaining the pH at 9.5 by 2M solution of NaOH. After the precipitation was complete, the slurry was placed in a reflux condenser for 8h at 80˚C for agitation and to allow growth and nucleation of the particles. When removed, the slurry was centrifuged thrice at 5000rpm for 10 minutes and washing was done with distilled water each time. The solid was then dried and for 5 hours at 80˚C in oven. (Fig 1). The LDH precursors were then heated in the muffle furnace of 6hours at 600˚C to obtain the mixed metal oxides.
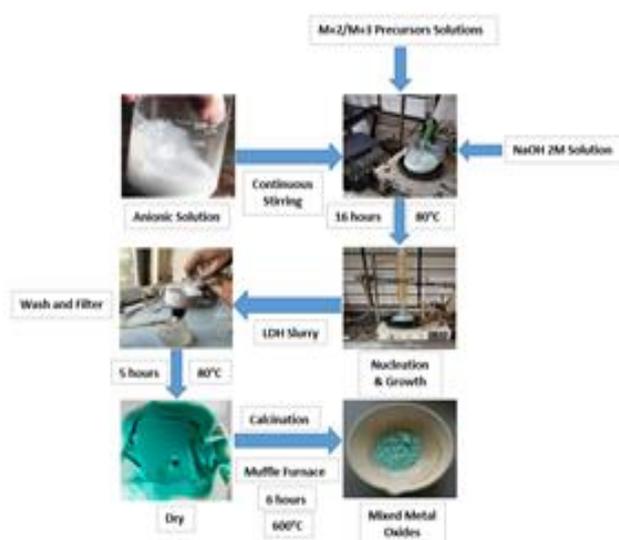
Fig. 1: Preparation of mixed metal oxide catalyst

D. Catalytic Application of Mixed Metal Oxides (MMO)

Approximately 236,000 g/mol commercial level polystyrene with molecular weight (MW) and 1.95wt index poly disparity was obtained from local market in Lahore. 0.5g of crushed polystyrene with 0.25g of $Ni_{0.25}Zn_{0.25}Al_{0.25}$ catalyst and 50mL of methanol was placed in an autoclave to react for 3h at 350˚C at continuous stirring. The same procedure was repeated for the other type of catalyst i.e. $Ni_{0.25}Cu_{0.25}Al_{0.25}$. Once the reaction was complete, the autoclave was cooled down and washed with a small amount of methanol to allow dissolution of any adsorbed products on the surface of the catalysts. The product mixture was then tested by GCMS.

III. RESULTS AND DISCUSSIONS

A. XRD Analysis

X-Ray diffraction patterns were scanned at 2θ= 20-60º. Major Intensity peaks for the $Ni_{0.25}Cu_{0.25}Al_{0.25}$ catalyst were observed at 27.42˚, 32.70˚, 36.12˚, 37.84˚, 39.16˚,43.50˚ 49.46˚and 60.01˚. A high degree of crystallinity was observed. In figure, Al_2O_3 was observed at 27.42º, 49.46º and 60.01º. where HKL values (012), (024) and (018) respectively. It was compared with ICDD card no 00-010-173[13]. CuO was witnessed at 32.70˚, 36.12˚and 39.16˚. where HKL values (100), (002) and (111) respectively. It was compared with JCPDS card no 00-041-0254[14]. NiO was confirmed at 37.84˚, and 43.50˚ where HKL value were (101) and (012) respectively[15].Due to the near proximity of the XRD patterns of NiO and CuO, it was challenging to separate NiO peaks from CuO. Major Intensity peaks for the $Ni_{0.25}Zn_{0.25}Al_{0.25}$ catalyst were observed at 28.25˚, 31.84˚, 36.12˚, 38.04˚, 45.15˚and 56.78˚. In comparison to Ni-Cu-Al catalyst, relatively a less degree of crystallinity was witnessed. In figure, Al_2O_3 was observed at 28.25º where HKL value (012). ZnO was seen at 31.84˚and 45.15˚ where HKL values (002) and (102) respectively. It was compared with JCPDS card no 36-1451[16]. NiO was confirmed at 38.04 where hkl value (101). A shift in the peak intensity may correspond to the demand of different calcinations temperature required for the crystallinity of each phase. A distinctive $Al_2O_3$was not observed clearly seen in the diffractogram. The crystallite size however seems to be small in case of $Ni_{0.25}Zn_{0.25} Al_{0.25}$ offering better surface area for catalysis. The distinction in crystallinity can be easily studied by in-situ analysis of evolution of the phase as per the rise in the calcination temperature.
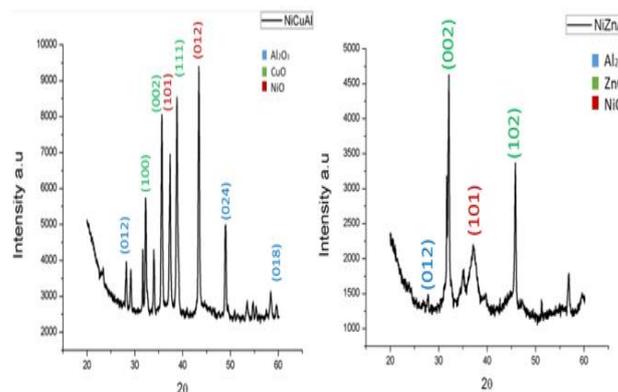
Fig. 2: Diffractogram of $Ni_{0.25}Cu_{0.25}Al_{0.25}$ catalyst and $Ni_{0.25}Zn_{0.25}Al_{0.25}$ catalyst at pH 9.5 at 600ºC

B. SEM Analysis

In Fig 3, part (a) and (b) indicate the morphology of $Ni_{0.25}Cu_{0.25}Al_{0.25}$uncalcined/as-prepared catalyst. The micrographs indicate round, porous lamellar structure with uniform composition and crystallinity. No defects and amorphous material can be observed. The LDH precursor is well-formed in layered structure. Likewise, (c) and (d) indicate the morphology of $Ni_{0.25}Zn_{0.25}Al_{0.25}$uncalcined/as-prepared catalyst. However, in this case, as explained before with the XRD, the structure of the precursor LDH and calcined was disrupted and cracked. The micrographs did

indicate some round, porous lamellar structure with only little uniformity in composition and crystallinity. Major defects and amorphous material can be observed. The LDH precursor has smaller particle size but layered structure is not definite.
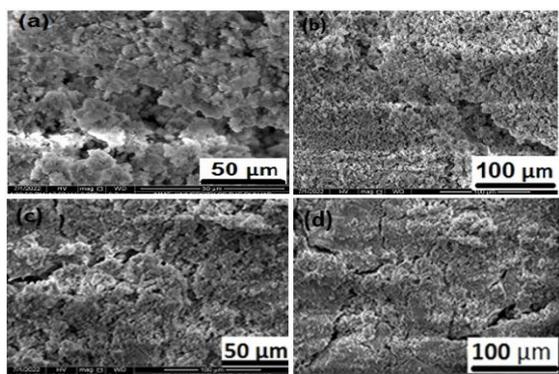
Fig.4: SEM images of $Ni_{0.25}Cu_{0.25}Al_{0.25}$ and $Ni_{0.25}Zn_{0.25}Al_{0.25}$

C. Energy Dispersive X-Ray Analysis (EDX)

➤ *Precipitation Profile of Uncalcined $Ni_{0.25}Cu_{0.25}Al_{0.25}$*

The Energy Dispersive X-ray Analysis was done to calculate the atomic percentages of actually precipitated metals in the LDH precursors. The data was calculated at 3 different spots of the samples to ensure amorphous and crystalline phase uniformity in deposition of metals. Figure 4 demonstrates the spot 1 of $Ni_{0.25}Cu_{0.25}Al_{0.25}$. The atomic percentages of various elements as determined by the EDX studies are listed in Table 1.
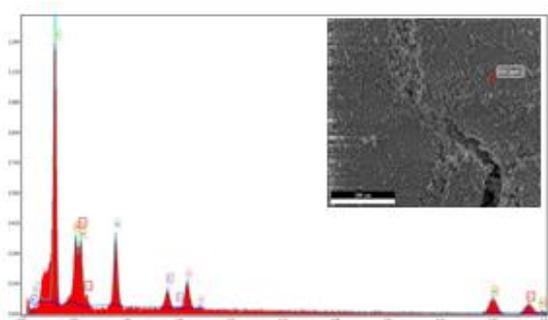
Fig. 4: Percentage of elements from EDX spot 1 of $Ni_{0.25}Cu_{0.25}Al_{0.25}$

Table 1: Percentage of elements from EDX spot 1 of $Ni_{0.25}Cu_{0.25}Al_{0.25}$

Element	Weight %	Atomic %	Net Int.
O	40.39	65.05	303.94
Ni	16.67	7.32	51.64
Cu	20.4	8.27	55.52
Al	11.77	11.24	85.07
H	3.8	3.06	25.57
C	6.97	5.07	40.43

Figure 5 demonstrates the spot 2 of $Ni_{0.25}Cu_{0.25}Al_{0.25}$ The atomic percentages of various elements as determined by the EDX studies are listed in Table 2.
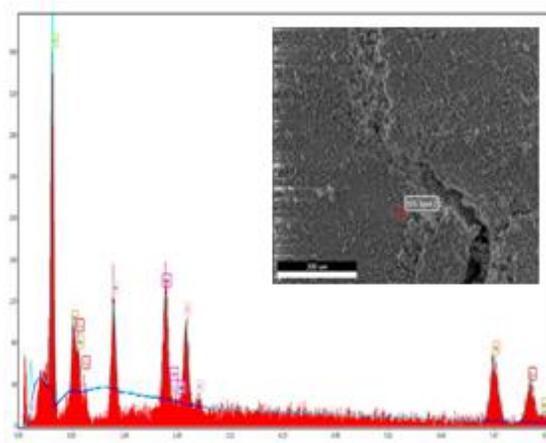
Fig. 5: Percentage of elements from EDX spot 2 of $Ni_{0.25}Cu_{0.25}Al_{0.25}$

Table 2: Percentage of elements from EDX spot 2 of $Ni_{0.25}Cu_{0.25}Al_{0.25}$

Element	Weight %	Atomic %	Net Int.
O	41.02	63.2	105.2
Ni	11.45	4.81	13.6
Cu	13.83	5.36	15.71
Al	11.91	10.88	37.13
H	8.26	6.35	22.73
C	13.54	9.41	31.22

Figure 6 demonstrates the spot 3 of $Ni_{0.25}Cu_{0.25}Al_{0.25}$ The atomic percentages of various elements as determined by the EDX studies are listed in Table 3.
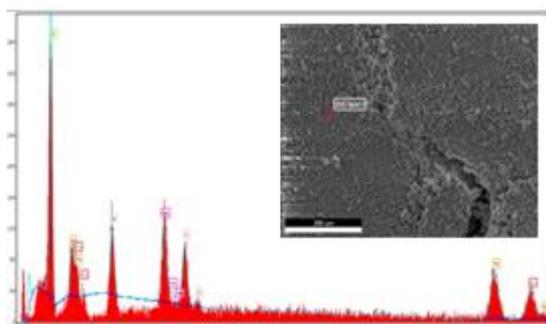
Fig. 6: Percentage of elements from EDX spot 3 of $Ni_{0.25}Cu_{0.25}Al_{0.25}$

Table 3: Percentage of elements from EDX spot 3 of $Ni_{0.25}Cu_{0.25}Al_{0.25}$

Element	Weight %	Atomic %	Net Int.
O	41.55	70.1	77.16
Ni	9.89	4.55	9.84
Cu	7.05	3	7.07
Al	7.15	7.15	21.58
H	22.84	6.43	31

The three spots taken in EDX is to determine the actual precipitation of metals in hydroxide form i.e. $Ni(OH)_2$, $Cu(OH)_2$ and $Al(OH)_3$. In this regard the 3 values taken for each metal will be counted as an average for better

estimation of precipitation (Table 4) of ideal total precipitation of metals: atomic percentage should be equal to the actual amount of incorporated at the time of coprecipitation.

Table 4: Average of each metal in $Ni_{0.25}Cu_{0.25}Al_{0.25}$

Metal Ion	Atomic Percentage (%)			Average
	Spot 1	Spot 2	Spot 3	
Ni	7.32	4.81	4.55	5.56
Cu	8.27	5.36	3	5.54
Al	11.24	10.88	7.15	9.75

Average atomic percentage of all metals in $Ni_{0.25}Cu_{0.25}Al_{0.25}$ Spot 1,2,3 = 5.56 (Ni)+ 5.54 (Cu) + 9.75 (Al) = 20.85

Average precipitation of Ni^{+2}=5.56/20.85=0.26 Average precipitation of Cu^{+2}=5.54/20.85=0.26 Average precipitation of Al^{+3}=9.75/20.85=0.46

Given above the molar ratios deposited in LDH, it seems that the average of the metal used in coprecipitation process and after the formation of LDH seems quite in correspondence which indicates the successful formation of the desired precursor. The fluctuation of the values in Al is attributed to the difference of pH required for formation of $Al(OH)_3$. It is to be taken into account that the mixed metal oxides (MMO) formed after calcination at higher temperatures have the same values of metal precipitation. Therefore, results of mixed metal oxides have not be mentioned in here.

1. Precipitation Profile of Un-calcined $Ni_{0.25}Zn_{0.25}Al_{0.25}$

The $Ni_{0.25}Zn_{0.25}Al_{0.25}$ LDH as determined by EDX at room temperature. The spectrum shows that all of the chemical components Al, Zn, Ni, and O, H are present in the produced samples, proving that no unified elements were lost during the annealing process but that there were no contaminants. However, as already explained by XRD and SEM images, this catalyst was observed to show poor crystallinity (Fig. 3c) and cracks (Fig. 3d). Similarly, EDX result indicated poor precipitation profile of this LDH, and the obtained does not correspond to the initial concentration of metals used as shown in by the average calculated in Table 8.

Figure 7 demonstrates the spot 1 of $Ni_{0.25}Zn_{0.25}Al_{0.25}$. The atomic percentages of various elements as determined by the EDX studies are listed in Table 5.
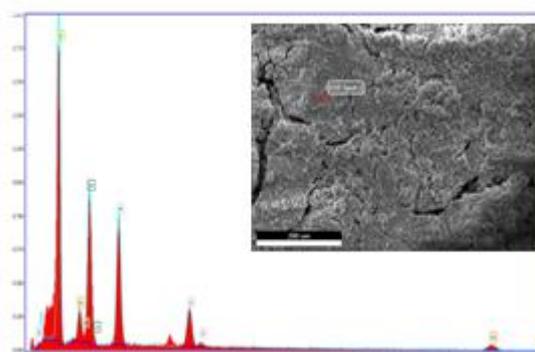
Fig. 7: Percentage of elements from EDX spot 1 of $Ni_{0.25}Zn_{0.25}Al_{0.25}$

Table 5: Percentage of elements from EDX spot 1 of $Ni_{0.25}Zn_{0.25}Al_{0.25}$

Element	Weight %	Atomic %	Net Int.
O	37.97	62.32	419.76
Ni	4.98	2.23	25.75
Zn	31.88	12.81	170.14
Al	17.19	16.73	192.96
C	7.98	5.91	73.19

Figure 8 demonstrates the spot 2 of $Ni_{0.25}Zn_{0.25}Al_{0.25}$. The atomic percentages of various elements as determined by the EDX studies are listed in Table 6.
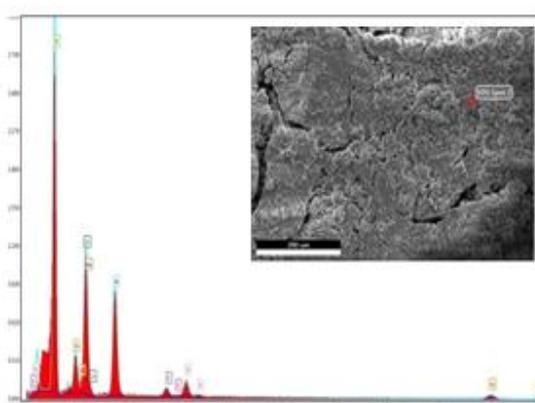
Fig. 8: Percentage of elements from EDX spot 2 of $Ni_{0.25}Zn_{0.25}Al_{0.25}$

Table 6: Percentage of elements from EDX spot 2 of $Ni_{0.25}Zn_{0.25}Al_{0.25}$

Element	Weight %	Atomic %	Net Int.
O	38.1	60.84	616.40
Ni	7.88	3.24	52.89
Zn	24.9	8.13	171.32
Na	3.45	8.6	79.81
Al	14.9	13.50	254.03
H	1.5	1.16	25.64
C	3.41	2.01	40.81

Figure 9 demonstrates the spot 3 of $Ni_{0.25}Zn_{0.25}Al_{0.25}$. The atomic percentages of various elements as determined by the EDX studies are listed in Table 7.
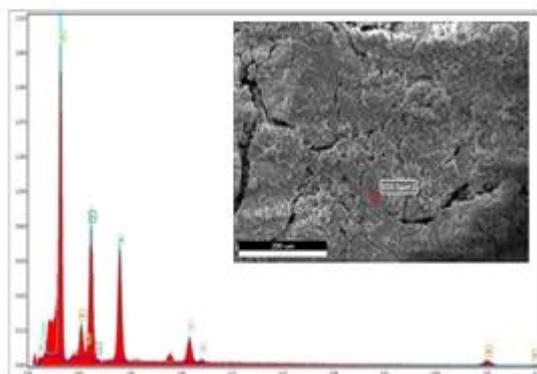
Fig. 9: Percentage of elements from EDX spot 3 of $Ni_{0.25}Zn_{0.25}Al_{0.25}$

Table 7: Percentage of elements from EDX spot 3 of $Ni_{0.25}Zn_{0.25}Al_{0.25}$

Element	Weight %	Atomic %	Net Int.
O	39.92	61.81	674.88
Ni	7.17	3.02	50.99
Zn	25.26	9.57	181.13
Na	7.06	7.6	77.85
Al	15.92	14.61	245.25
H	1.5	1.16	21.52
C	3.18	2.22	39.91

The three spots taken in EDX is to determine the actual precipitation of metals in hydroxide form i.e. $Ni(OH)_2$, $Zn(OH)_2$ and $Al(OH)_3$. In this regard the 3 values taken for each metal will be counted as an average for better estimation of precipitation. (Table 8)

Table 8: Average of each metal in $Ni_{0.25}Zn_{0.25}Al_{0.25}$

Metal Ion	Atomic Percentage (%)			Average
	Spot 1	Spot 2	Spot 3	
Ni	2.23	3.24	3.02	2.83
Zn	12.81	8.13	9.57	10.17
Al	16.73	13.50	14.61	14.9

As discussed before, in case of ideal total precipitation of metals: atomic percentage should be equal to the actual amount of incorporated at the time of coprecipitation. So, here in the same way, the deposition of Nickel, Zinc and Aluminum has been calculated.

Average atomic percentage of all metals in $Ni_{0.25}Zn_{0.25}Al_{0.25}$ Spot 1,2,3 = 2.83 (Ni)+ 10.17 (Zn) + 14.9 (Al) = 27.9

Average precipitation of Ni^{+2}=2.83/27.9=0.10
Average precipitation of Zn^{+2}=10.17/27.9=0.36
Average precipitation of Al^{+3}=14.9/27.9=0.53

Given above the molar ratios deposited in LDH, it seems that the average of the metal used in coprecipitation process and after the formation of LDH seems to have major difference in the values which indicates the deformation/leaching and defects in LDH precursor. The

fluctuation of the values in Ni and Al is attributed to the combined difference of pH required for formation of $Zn(OH)_2$ and $Al(OH)_3$. As reported $Al(OH)_3$ is the first layer to form in the LDH, deformation in this layer can cause the further defects in lamellar hydroxide formation{Grégoire, 2013 #11}.It is to be taken into account that the mixed metal oxides (MMO) formed after calcination at higher temperatures have the same values of metal precipitation. Therefore, results of mixed metal oxides have not be mentioned in here.

D. Catalytic Reaction and Analysis by GC-MS

After the reaction run time, the autoclave was allowed to cool down for an hour before opening it. The reaction product was washed by 5mL of methanol to allow any undissolved products on the walls of the autoclave and on the magnetic stirrer. Prior to the analysis by GCMS, the samples were micro-filtered. Column: ZB-5HT Length=15m,thickness=0.10um,diameter=0.25mm; Column oven temperature=40°C;Injection Temperature=250°C; Carrier gas: He, Column flow =1.51mL/min; Total flow =8.5mL/min; Split=10; Total program time=30min.Low molar mass compounds were separated. These were found by comparing their mass spectral fragmentation patterns and retention indices to those in the public domain mass spectral library and the version 2 spectral library from the National Institute of Standards and Technology.

1. Catalytic Reaction by $Ni_{0.25}Cu_{0.25}Al_{0.25}$ Mixed Oxides

Figure 10 demonstrates the fragmentation of Polystyrene. The chromatogram obtained by the catalytic hydrogenation of Polystyrene at 350˚C is shown in Fig 10(a). Three distinct peaks at RT 4.20min, 8.32min and 9.86min were observed. Peak at 4.20min corresponds to the solvent (MeOH), Peak at 8.32min shows the molecular ion (M^+) at 84=(m/z); peak at 9.86 corresponds to the molecular ion (M^+)=154 (m/z). The peak at 84 represent the cyclohexane (C_6H_{12}). The aromaticity of the Polystyrene remains intact. However, the conjugation disappeared and the benzene ring was converted into cyclohexane as shown in figure below {Fig. 10(b)}. The molecular peak of (M^+) at 154=(m/z) indicates the fragmentation of Polystyrene to Benzene ring with 5 Carbon (CH_2-CH_3 chain).
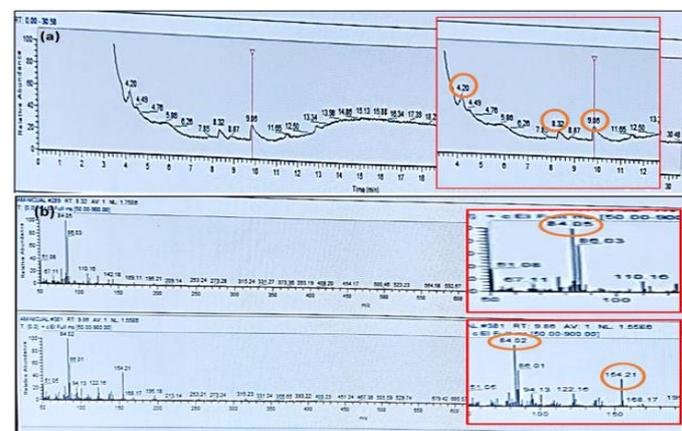
Fig. 10:(a) shows the retention time of the products, (b) shows the total ion chromatograph of the products of

catalytic reaction by $Ni_{0.25}Cu_{0.25}Al_{0.25}$ mixed oxides; Temp=350ºC

2. Catalytic Reaction by $Ni_{0.25}Zn_{0.25}Al_{0.25}$ Mixed Oxides

Figure 11(a) demonstrates the fragmentation of Polystyrene by Catalytic Reaction by $Ni_{0.25}Zn_{0.25}Al_{0.25}$ Mixed Oxides. Three distinct peaks at RT 4.04min, 8.09min and 9.31min were observed. Peak at 4.04min corresponds to the solvent (MeOH), Peak at 8.09min shows the molecular ion (M^+) at 84.02=(m/z); peak at 9.31 corresponds to the molecular ion (M^+) =154 (m/z). The peak at 84.00 represent the cyclohexane (C_6H_{12}). Even in this case, the aromaticity of the Polystyrene remained intact. However, the conjugation disappeared and the benzene ring was converted into cyclohexane as shown in figure below {Fig. 11(b)}. The molecular peak of (M^+) at 154= (m/z) indicated the fragmentation of Polystyrene to Benzene ring with 5 Carbon $(CH_2-CH_3$ chain).
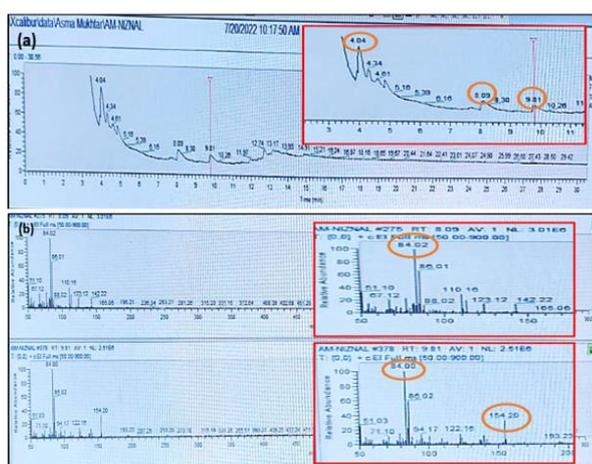
Fig. 11:(a) shows the retention time of the products, (b) shows the total ion chromatograph of the products of catalytic reaction by $Ni_{0.25}Zn_{0.25}Al_{0.25}$ Mixed Oxides; Temp=350ºC

IV. CONCLUSIONS

Ni-Cu-Al and Ni-Zn-Al LDH precursors were produced by the coprecipitation method to obtain mixed transition metal oxides (MMO). The catalysts were successfully characterized by XRD, SEM and EDX which showed great crystallinity and presence of no amorphous phase in Ni-Cu-Al LDH precursors. However, in case of Ni-Zn-Al, the structure of the catalyst was seen disturbed and cracked as per the SEM micrographs. Moreover, the EDX results also showed the unjustified precipitation of molar concentration in Ni-Zn-Al catalysts. These MMO were then used for the catalytic application i.e. fragmentation of Polystyrene to smaller products at 350˚C in the presence of hydrogen donor solvent, Methanol. To our surprise, extremely interesting results were achieved. In the presence of MeOH at 350˚C, cyclohexane was produced by both catalysts indicating that MeOH is a powerful hydrogenation solvent in this case because it deconjugated the benzene ring. Though as reported before, the Ni-Zn-Al LDH (in precursor form) had defects but after its calcination at 600˚C, the formed mixed oxides just as perfect as Ni-Cu-Al

catalyst. Polystyrene is a tough polymer to degrade at such gentle conditions. In this work, we suggested a relatively less harsh method to degrade this polymer in comparison to pyrolysis (450˚C <) and produce a platform chemical, cyclohexane which can be easily utilized for the production of several other compounds. In future Prospective, to Study of other hydrogen-donor solvents under the same and different conditions to find greener conditions for the fragmentation. To study the effect of mixed oxides calcined at different temperatures and relative products produced. To investigate degradation of other polymers such as Polyurethane and PET by this method. Calculation of carbon balance and total conversion in the process would be of great benefit.

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