Ravi Shanker Ahuja, Annabathini Geetha Bhavani, Tanveer Ahmad Wani, Tara Prasad*

School of Sciences, Noida International University, Greater Noida, India

Scientific paper
ISSN 0351-9465, E-ISSN 2466-2585
https://doi.org/10.62638/ZasMat1178

Zastita Materijala 65 (3)
403 - 407 (2024)

Effect of Ni content over Ni-Mg-Al hydrotalcite structure

ABSTRACT

Hydrotalcite powder materials have well demanded applications in various fields. The Ni-Mg-Al hydrotalcite materials are prepared through co-precipitation method by varying the Ni amounts. The Ni ratios of 0.1, 0.2, 0.3 and 0.4 results the materials of $Ni_{0.1}Mg_{0.60}Al_{0.34}$, $Ni_{0.2}Mg_{0.60}Al_{0.34}$, $Ni_{0.3}Mg_{0.40}Al_{0.34}$, $Ni_{0.4}Mg_{0.30}Al_{0.34}$ are obtained at pH of 9.3. The calcined hydrotalcite materials are analyzed through BET, XRD and SEM. The observations are well in correlation between the materials. Increase in Ni amount of 0.2 leads the optimum level of loading in hydrotalcite structure which may lead the inter-layer platelets spacing and reduces the surface area.

Keywords: *Hydrotalcite materials; Synthesis; Nickel; Characterization*

1. INTRODUCTION

Hydrotalcite (HT) synthetic materials are known as layered double hydroxides. HT powdered materials are having wide range of real time applications in pharmaceuticals, as a catalyst, polymer-composite materials, absorbents, impurities removal, wastewater treatment, polymers, building materials and many more [1-3]. HT layered structures may also help in combination of different metal ions, which is useful active site for a material as catalyst. HT materials are used to maintain pH value of the substance, therefore, used in cosmetic, pharmacy and beauty products. The applications are raising the demand of high grade hydrotalcite materials with low cost and simple production methods. HT materials are clay-type consist of anions with the formula of $M_{1-X2}+M_{x3}+(OH)(2An-)_{x/n}.yH_2O$. The transition metals are comparable with Mg^{2+}, Ni^{2+}, Zn^{2+}, Cu^{2+}, Co^{2+}, Al^{3+}, Fe^{3+} and Cr^{3+} due to their ionic radius of around 0.5 - 0.8 Å [4]. The layers may charge positively by the substitution of metal ions of M^{3+} for M^{2+}. The HT materials are effectively synthesized using methods like hydrothermal, urea reduction method and microwave process. Among all methods the co-precipitation method is versatile, cost effective and simple to practice with parameters like controlled pH and controlled temperature [5-7].

Corresponding author: Annabathini Geetha Bhavani
E-mail: ageethabhavani@gmail.com
Paper received: 12.01.2024.
Paper accepted: 14. 02. 2024.
Paper is available on the website: www.idk.org.rs/journal

The precipitation method is highly tunable with respect to metal composition and perfect metal distribution is possible. Takehira et al. [8] prepared Ni-Mg-Al hydrotalcite using $EDTA^{4-}$ ligands with pre-complexation are found highly stable catalytic activity of dry reforming of methane. The Ni-Mg-Al with $EDTA^{4-}$ ligands provides the stability in conversion of methane and produced the effective production of syngas. Takehira [9] prepared selective replacement of Ni with Mg over Mg-Al hydrotalcite using low pH to form egg shell-type particles by memory-effect. Baltes et. al. [10] prepared the $Cu/ZnO/Al_2O_3$ by altering the synthesis parameters like pH of 6-8 and 70^0C temperature for methanol production.

The aim of this article was given optimal preparation for preparation Ni-Mg-Al hydrotalcite with the modification of synthesis metal composition by varying the Ni amount over Mg-Al hydrotalcite with keeping constant pH, precipitating agent and temperature. The hydrotalcite material is characterized by XRD, BET, SEM to correlate the effect of Ni amount on crystallinity, surface area and crystal morphology.

2. EXPERIMENTAL

2.1. Chemical Reagents

All the chemical reagents are received from Sigma Aldrich-India with the purity of 99%. The analytical grade of $Ni(NO_3)_2{\cdot}6H_2O$, $Mg(NO_3)_2{\cdot}$ $\cdot 6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, Na_2CO_3, NaOH sodium dodecylbenzenesulfonate were used for synthesis of hydrotalcite powdered materials.

2.2. Synthesis of Hydrotalcite Powdered Material

The hydrotalcite powdered materials were synthesized through co-precipitation of chemical reagents with stoichiometric molar ratios. The metal precursors are dissolved for clear solution. The $Metal^{II}$ ion (Ni-Mg) with $Metal^{III}$ (Al) ratios in the formula of $Ni_XMg_{0.70-X}Al_{0.34}$ $(OH)_2(CO_3)_{0.19}.mH_2O$ was varying the X amount (Ni) = 0.1, 0.2, 0.3 and 0.4 were synthesized. The precipitating agents with molar ratios are prepared in standard flask for effective co-precipitation. The pH, temperature of the super-saturation solution is strictly monitored for homogeneous precipitation. In all ratios precipitating agent is kept common by varying the metal salt (Ni) as shown in flow chart in Fig.1 and Table 1. All the samples were aged for 4 hours of continuous stirring at pH of 9.3. The precipitate was dried in hot air oven for 24 hours at 120 °C. The dried cake was grinded to fine powder before calcination. The resulted samples are denoted as $Ni_{0.1}Mg_{0.60}Al_{0.34}$, $Ni_{0.2}Mg_{0.60}Al_{0.34}$, $Ni_{0.3}Mg_{0.40}Al_{0.34}$, $Ni_{0.4}Mg_{0.30}Al_{0.34}$. The powdered hydrotalcite materials are fired in air at 600 °C for 2 hours and stored in desiccator for characterization.

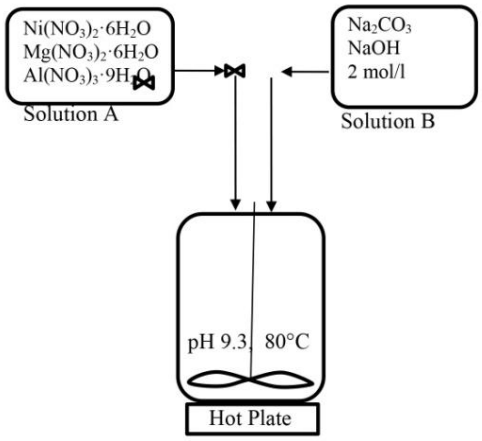

Figure 1. Flow chart of hydrotalcite synthesis by Co-precipitation method

2.3. Characterization of powdered hydrotalcite materials

The synthesis parameters are the empirical and reviewed for critical change in physical characteristics like crystallinity, phases purity, surface area, pore volume, crystal morphology, particle size as per our earlier experimental articles [11-13]. Many researchers are still optimizing the synthesis parameters for desired crystal size. Kühl et al. [7,8] screened the Cu/ZnAlOx hydrotalcite for phase purity and pore volume using XRD and BET analysis with prior to catalytically application. Baltes et al. [10] characterized the $Cu/ZnO/Al_2O_3$ catalysts with XRD for precipitate phases and dispersion of Cu metal and surface area to evaluate the synthesis parameters. They found correlations between the synthesis parameters are directly proportional to physical characteristics like crystallinity and surface area and metal dispersion and even the catalytic performance.

3. RESULTS AND DISCUSSION

3.1. Brunauer-Emmett-Teller (BET) analysis observations

BET was performed over $Ni_{0.1}Mg_{0.60}Al_{0.34}$, $Ni_{0.2}Mg_{0.60}Al_{0.34}$, $Ni_{0.3}Mg_{0.40}Al_{0.34}$, $Ni_{0.4}Mg_{0.30}Al_{0.34}$ HT materials and result are expedited in Table 1. The prepared samples are found to be improved with surface area, pore volume and pore cross section. The results obtained for $Ni_{0.1}Mg_{0.60}Al_{0.34}$ are very pleasant, with surface area as high as 53.01 m^2/g, pore volume is 6.521 CC/g. $Ni_{0.2}Mg_{0.60}Al_{0.34}$ gives surface area 55.243 and pore volume 7.009CC/g. $Ni_{0.3}Mg_{0.40}Al_{0.34}$ surface area is 42.84 m^2/g and pore volume 5.378 CC/g. $Ni_{0.4}Mg_{0.30}Al_{0.34}$ material gives surface area 38.58 m^2/g with pore volume 2.805 CC/g. Compared to all the amounts of Ni loading $Ni_{0.2}Mg_{0.60}Al_{0.34}$ found highest surface area and pore volume is due to the weight loss and to reduction of platelets [14]. The pore volume and surface area decreasing with respective of amount of Ni loading in replacement of Mg^{2+} structure may have affected by platelets space between the average inter-particles.

3. 2. Analysis of XRD reflections

HTs materials prepared through co-precipitation of $Ni_{0.1}Mg_{0.60}Al_{0.34}$, $Ni_{0.2}Mg_{0.60}Al_{0.34}$, $Ni_{0.3}Mg_{0.40}Al_{0.34}$, $Ni_{0.4}Mg_{0.30}Al_{0.34}$ are examined by XRD reflections. The range of crystal diffraction are between 2 θ to 80 θ was observed. All materials are shown in Fig. 2 and not found any other crystal phases, either formation of by-product reflections are not observed. The conformation of hydrotalcite structure of peaks are observed at 26° (006), 37° represent the phase (111), 43-47° represent the phase (200), 62-63° represent the phase (220) respectively. The sharp, intense peaks confirm the highly crystalline and crystal are in small sizes. The peaks intensity decreases with increasing the Ni loading from $Ni_{0.1}$ to $Ni_{0.4}$. The solid solutions formation reflects the phase of NiO, MgO, $NiAl_2O_4$, $MgAl_2O_4$. The peak at 47 θ° represent the NiO phase [47-1049], 63 θ° MgO phase [65-0476], at 74 θ° Mg_2O_4 phase [74-1132] respectively. XRD analysis reflects high intensity of the peaks over $Ni_{0.2}Mg_{0.60}$ $Al_{0.34}$ with comparison of $Ni_{0.1}Mg_{0.60}Al_{0.34}$, $Ni_{0.3}Mg_{0.40}Al_{0.34}$, $Ni_{0.4}Mg_{0.30}Al_{0.34}$ HT materials. Martínez et al. [15] observed Ni particles size of 10 nm of Ni-Al-La. Juan-Juan et al. [16] reported various pre-treatment methods for optimising Ni particles sizes of 6.3 and 7.8 nm over Ni/Al_2O_3. Takehira et. al. [8,9] and Perez-Lopez et al. [21], reported the various synthesis parameter to achieve the hydrotalcite structure of $Ni/MgO/Al_2O_3$. The Table 1 depicts through reflections by peak-width analysis of full width half maximum (FWHM)

provides the 11–16 nm scale of NiO particles of $Ni_{0.1}Mg_{0.60}Al_{0.34}$, $Ni_{0.2}Mg_{0.60}Al_{0.34}$, $Ni_{0.3}Mg_{0.40}Al_{0.34}$, $Ni_{0.4}Mg_{0.30}Al_{0.34}$ HT materials. Indeed, the preparation of a series of hydrotalcite with different Ni loading may influence the structural change and physio-chemical properties [18].

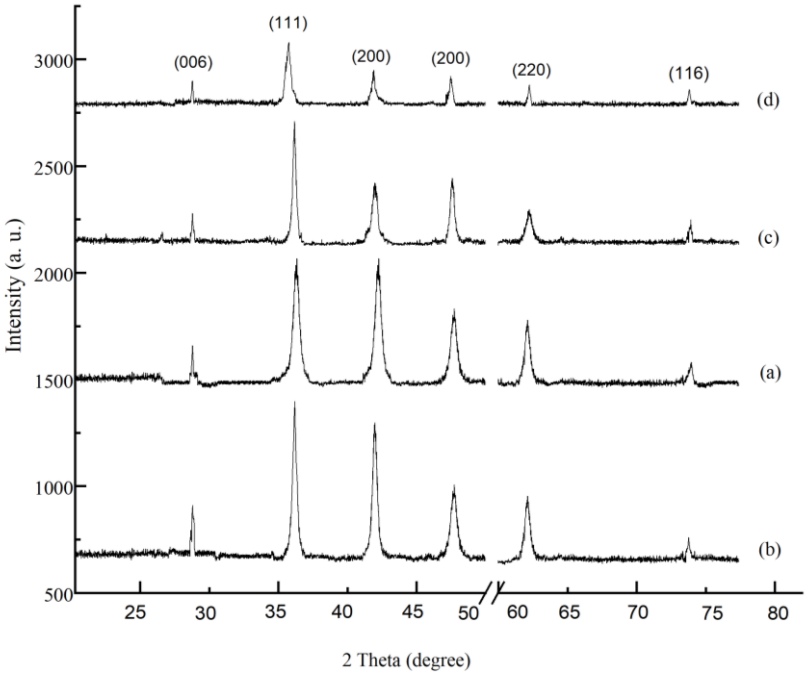

Figure 2. XRD patterns of hydrotalcite powered materials, (a) $Ni_{0.1}Mg_{0.60}Al_{0.34}$, (b) $Ni_{0.2}Mg_{0.60}Al_{0.34}$, (c) $Ni_{0.3}Mg_{0.40}Al_{0.34}$, (d) $Ni_{0.4}Mg_{0.30}Al_{0.34}$

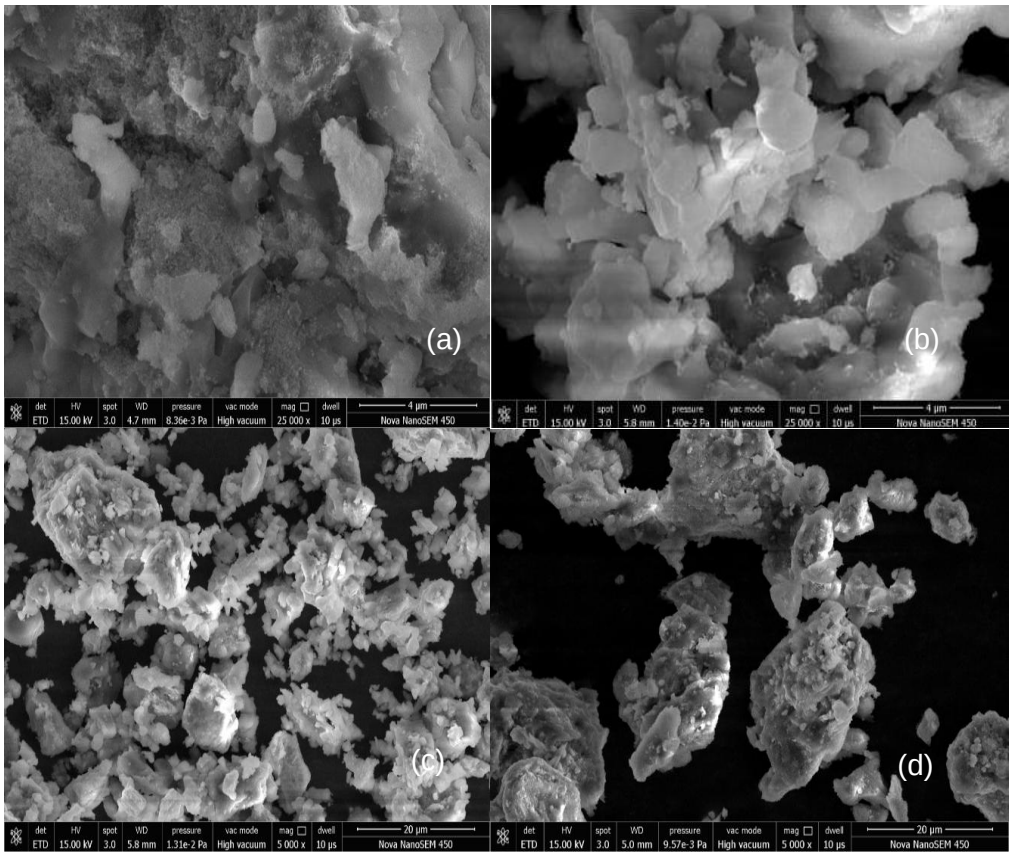

Figure 3. SEM images of hydrotalcite powered materials, (a) $Ni_{0.1}Mg_{0.60}Al_{0.34}$, (b) $Ni_{0.2}Mg_{0.60}Al_{0.34}$, (c) $Ni_{0.3}Mg_{0.40}Al_{0.34}$, (d) $Ni_{0.4}Mg_{0.30}Al_{0.34}$

Table 1. Physicochemical Properties of the Ni-Mg-Al Hydrotalcite materials

HT Composition	Surface Area m^2/g[a]	Total Pore Volume CC/g[b]	Cross Section Area[c]	NiO Particle size m^2/g[d]
Ni0.1Mg0.60 Al0.34	53.01	6.521	11.2 A°	11.7
Ni0.2Mg0.60 Al0.34	55.43	7.009	16.2 A°	11.5
Ni0.3Mg0.40 Al0.34	42.84	5.378	9.4 A°	14.8
Ni0.4Mg0.30 Al0.34	38.58	2.805	5.1 A°	16.3

[a], [b], [c] - Received from BET analysis; [d] - Calculated from peak full width half maximum (FWHM) through Origin software.

3.3. Morphology observations from SEM analysis

The morphology of all the samples are crystalline and platelet like structure. Fig. 3 of the $Ni_{0.1}Mg_{0.60}Al_{0.34}$, $Ni_{0.2}Mg_{0.60}Al_{0.34}$, $Ni_{0.3}Mg_{0.40}Al_{0.34}$, $Ni_{0.4}Mg_{0.30}Al_{0.34}$ HT materials morphology is significantly clear by crystal edges. Compared to other Ni amounts (0.1, 0.3, 0.4), the Ni amount of 0.2 ($Ni_{0.2}Mg_{0.60}Al_{0.34}$) shows the definite stacked brucite-like sheets with hexagonal structure. XRD reflections of $Ni_{0.2}Mg_{0.60}Al_{0.34}$ also confirm the low particle size (Table 1). Whereas good argument with the result of surface area of the material $Ni_{0.2}Mg_{0.60}Al_{0.34}$ is found to be highest (55.423 m^2/g) among the all HT powered materials [19-22].

4. CONCLUSION

Hydrotalcite powered materials are having significant industrial applications. The requirement of highly crystalline hydrotalcite material with low cost is the quest. This article was aimed to prepare Ni-Mg-Al hydrotalcite material by varying the Ni amounts. The hydrotalcite materials are prepared $Ni_{0.1}Mg_{0.60}Al_{0.34}$, $Ni_{0.2}Mg_{0.60}Al_{0.34}$, $Ni_{0.3}Mg_{0.40}Al_{0.34}$, $Ni_{0.4}Mg_{0.30}Al_{0.34}$ through co-precipitation method. The precursors are precipitated with Na_2CO_3, NaOH at pH of 9.3 followed by drying and calcination. The materials $Ni_{0.1}Mg_{0.60}Al_{0.34}$, $Ni_{0.2}Mg_{0.60}Al_{0.34}$, $Ni_{0.3}Mg_{0.40}Al_{0.34}$, $Ni_{0.4}Mg_{0.30}Al_{0.34}$ are obtained. The BET analysis provides the potential surface area and pore volume of all the HT materials. The XRD analysis has significant insights of the synthesized materials as phase purity of hydrotalcite structure confirmation. The SEM analysis confirms the brucite layered structure. Compared to all, the $Ni_{0.2}Mg_{0.60}Al_{0.34}$ shown highest surface area and lowest particle size.

Acknowledgement

We acknowledge the funding agency 'Agricom Food Pvt Ltd Mumbai' for supporting this research project.

5. REFERENCES

[1] R.Trujillano, F.Labajos, V.Rives (2023) Hydrotalcites, a rapid survey on the very recent synthesis and applications procedures, *Applied Clay Science*., 238, 106917-106927. https://doi.org/10.1016/j.clay.2023.106927

[2] B.Wiyantoko, P.Kurniawati, T.E.Purbaningtias, I.Fatimah (2015) Synthesis and Characterization of Hydrotalcite at Different Mg/Al Molar Ratios, *Procedia Chemistry*., 17, 21-26, https://doi.org/10.1016/j.proche.2015.12.115

[3] C.Forano, T.Hibino, F.Leroux, G.Ho, in: Bergaya, F., Theng, B.K.G., Lagaly (2006) Developments in clay science*, Elsevier, Amsterdam*. 1, 1021-1095 http://dx.doi.org/10.1016/S1572-4352(05)01001-9

[4] F.Cavani, F.Trifirò, A.Vaccari (1991) Hydrotalcite-type anlonlc clays: preparation, properties and applications, *Catalysis Today*, 11, 173-301, https://doi.org/10.1016/0920-5861(91)80068-K

[5] Recommendations on Nomenclature for Contamination Phenomena in Precipitation from Aqueous Solutions (1974) *International union of pure and applied chemistry*., 37, 463-468, https://doi.org/10.1351/pac197437040463

[6] F.Schüth, M.Hesse, K.K.Unger, G.Ertl, H. Knoezinger, J.Weitkamp (2008) *Handbook of Heterogeneous Catalysis, 2nd Edition*, p.100-119.

[7] A.I.Tsyganok, T.Tsunoda, S.Hamakawa, K.Suzuki, K.Takehira, T.Hayakawa (2003) Dry reforming of methane over catalysts derived from nickel-containing Mg-Al layered double hydroxides, *Journal of catalysis.,* 213, 191-203, doi:10.1016/S0021-9517(02)00047-7

[8] Y.J. Zhang, R.G. Evans (2012) Alignment of layered double hydroxide platelets, *Colloids Surf A Physicochem Eng Asp*., 408, 71-78. https://doi.org/10.1016/j.colsurfa.2012.05.033

[9] K.Takehira, T.Kawabata, T.Shishido, K.Murakami, T.Ohi, D.Shoro, M.Honda, K.Takaki (2005) Mechanism of reconstitution of hydrotalcite leading to eggshell-type Ni loading on MgAl mixed oxide, *J.Catal*, 231, 92-104. https://doi.org/10.1016/j.jcat.2005.01.025

[10] C.Baltes, S.Vukojević, F.Schüth, J.Catal (2008) Correlations between synthesis, precursor, and catalyst structure and activity of a large set of $CuO/ZnO/Al_2O_3$ catalysts for methanol synthesis, *Journal of Catalysis*., 258, 334-344. https://doi.org/10.1016/j.jcat.2008.07.004

[11] A.G.Bhavani, W.Y.Kim, J.Y.Kim, J.S.Lee (2013) Improved activity and coke resistance by promoters of nanosized trimetallic catalysts for autothermal carbon dioxide reforming of methane, *Applied Catalysis A: General.,* 450, 63-72. https://doi.org/10.1016/j.apcata.2012.10.008

[12] A.G.Bhavani, W.Y.Kim, J.W.Lee, J.S.Lee (2015) Influence of Metal Particle Size on Oxidative CO_2 Reforming of Methane over Supported Nickel Catalysts: Effects of Second-Metal Addition, *ChemCatChem.,* 7(9), 1445-1452, https://doi.org/10.1002/cctc.201500003

[13] A.G.Bhavani, W.Y.Kim, J.S.Lee (2018) Autothermal CO_2 Reforming with Methane Over Crystalline $LaMn_{1-X}Ni_XO_3$ Perovskite Catalysts, *ACS Catalysis.,* 3 (7), 1537-1544, doi:10.35840/2631-5076/9210

[14] A.G.Bhavani, T.A.Wani, A.Ma'aruf, T.Prasad (2021) Effect of ageing process on crystal morphology of Co-Mg-Al hydrotalcite, *Materials Today: Proceedings.,* 44, 2277-2282, doi:10.1016/j.matpr.2020.12.390

[15] R.Martínez, E.Romero, C.Guimon, R.Bilbao (2004) CO_2 reforming of methane over coprecipitated Ni-Al catalysts modified with lanthanum,*Applied Catalysis., A,* 274, 139-149. doi:10.1016/j.apcata.2004.06.017

[16] J.Juan-Juan, M.C.Román-Martínez, M.J.Illán-Gómez (2009) Nickel catalyst activation in the carbon dioxide reforming of methane: Effect of pretreatments, *Applied Catalysis A.* 55, 27-32, https://doi.org/10.1016/j.apcata.2008.10.058

[17] O.W.Perez-Lopez, A.Senger, N.R.Marcilio, M.A.Lansarin (2006) Effect of composition and thermal pretreatment on properties of Ni–Mg–Al catalysts for CO_2 reforming of methane, *Applied Catalysis A*., 303, 234-244. https://doi.org/10.1016/j.apcata.2006.02.024

[18] T.Shishido, M.Sukenobu, H.Morioka, R.Furukawa, H.Shirahase, K.Takehira (2001) CO_2 reforming of CH_4 over Ni/Mg–Al oxide catalysts prepared by solid phase crystallization method from Mg–Al hydrotalcite-like precursors, *Catal. Lett.,* 73, 21-26.

[19] H.Huang Tay, Zhanhu Guo, Luwei Chen, Yan Liu, Ji e Chang, Ziyi Zhong, Jizhong Luo, Armando Borgna (2012) Morphology and composition controllable synthesis of Mg–Al–CO_3 hydrotalcites by tuning the synthesis pH and the CO_2 capture capacity, *Appl Clay Sci.,* 55, 18-26. https://doi.org/10.1016/j.clay.2011.07.024

[20] F.M.Labajos, V.Rives, M.A.Ulibarri (1992) Effect of hydrothermal and thermal treatments on the physicochemical properties of Mg-Al hydrotalcite-like materials, *J.Mater. Sci*., 27, 1546-1552 https://doi.org/10.1007/BF00542916

[21] M.Behrens, I.Kasatkin, S.Kühl, G.Weinberg (2010) Phase-Pure Cu,Zn,Al Hydrotalcite-like Materials as Precursors for Copper rich Cu/ZnO/Al_2O_3, Catalysts, *Chem. Mater*., 22, 386-397. https://doi.org/10.1021/cm9029165

[22] S.Kühl, A.Tarasov, S.Zander, I.Kasatkin, M.Behrens (2014) Cu-based catalyst resulting from a Cu,Zn,Al hydrotalcite-like compound: a microstructural, thermoanalytical, and in situ XAS study, *Chemistry European. Journal*., 20, 3782-3792, doi: 10.1002/chem.201302599

IZVOD

UTICAJ SADRŽAJA Ni NA STRUKTURU Ni-Mg-Al HIDROTALCITA

Hidrotalcitni praškasti materijali imaju veoma traženu primenu u različitim oblastima. Ni-Mg-Al hidrotalcitni materijali se pripremaju metodom ko-precipitacije variranjem količine Ni. Odnosi Ni od 0,1, 0,2, 0,3 i 0,4 rezultiraju da su materijali Ni0.1Mg0.60Al0.34, Ni0.2Mg0.60Al0.34, Ni0.3Mg0.40Al0.34, Ni0.4Mg0.30Al0.34 dobijeni pri pH od 9.3. Kalcinisani hidrotalcitni materijali se analiziraju putem BET, XRD i SEM. Zapažanja su u dobroj korelaciji između materijala. Povećanje količine Ni od 0,2 dovodi do optimalnog nivoa opterećenja u strukturi hidrotalcita što može dovesti do međuslojnog razmaka trombocita i smanjenja površine.
Ključne reči: *hidrotalcitni materijali; sinthesis; nickel; karakterizacija.*

Naučni rad
Rad primljen: 12. 01. 2024.
Rad prihvaćen: 14. 02. 2024.
Rad je dostupan na sajtu: www.idk.org.rs/casopis

Ravi Shanker Ahuja https://orcid.org/0009-0003-6441-6232
Annabathini Geetha Bhavani https://orcid.org/0000-0003-0258-5930
Tanveer Ahmad Wani https://orcid.org/0000-0001-5582-6190
Tara Prasad https://orcid.org/0000-0002-7499-5755