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MgAl-Layered Double Hydroxide Solid Base Catalysts for Henry Reaction: A Green Protocol

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Abstract: A series of MgAl-layered double hydroxide (MgAl-HT), the calcined form at 500 °C ($MgAlO_x$), and the rehydrated one at 25 °C (MgAl-HT-RH) were synthesized. Physicochemical properties of the catalysts were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Surface area of the as-synthesized, calcined, and rehydrated catalysts was determined by N_2 physisorption at −196 °C. CO_2 temperature-programmed desorption (CO_2-TPD) was applied to determine the basic sites of catalysts. The catalytic test reaction was carried out using benzaldehyde and their derivatives with nitromethane and their derivatives. The Henry products (1–15) were obtained in a very good yield using MgAl-HT-RH catalyst either by conventional method at 90 °C in liquid phase or under microwave irradiation method. The mesoporous structure and basic nature of the rehydrated solid catalyst were responsible for its superior catalytic efficiency. The robust nature was determined by using the same catalyst five times, where the product % yield was almost unchanged significantly.

Keywords: C–C bond formation; Henry reaction; solid base catalyst; layered double hydroxide

1. Introduction

The fine chemical industry has experienced remarkable interest over the past few years due to the high requirements for products like pharmaceuticals, pesticides, fragrances, flavorings, and food additives [1].

The classical methods for the C–C coupling in the Henry reaction using soluble bases such as alkali metal hydroxides, carbonates, bicarbonates, alkoxides, alkaline earth metal hydroxide, aluminium ethoxides, complexes, and also organic bases such as primary, secondary, and tertiary amines, usually resulted in dehydrated products [2]. Therefore, careful control of the basic properties of the reaction medium is vital to obtain better yields of β-nitroalcohols. However, the efforts done by the researchers in the literature required longer reaction times and produced moderate yields [3,4]. The stoichiometric organic synthesis that largely applied so far resulted in large quantities of inorganic salts as byproducts; the disposal of such material causes a serious problem due to the important environmental issues [5]. The homogenous catalytic methodologies reported in the literature have many disadvantages, such as disposal of waste and difficulty recovering the catalyst from the products. In the last decade, there were notable improvements in the development of heterogeneous catalysts for the Henry reaction [6].

The extraordinary growth in the industry's struggle has pushed researchers to advance more effective catalytic processes in the synthesis of fine chemicals. The products of the Henry reaction,

those representing C–C bond development, are substantial materials widely used in frequent organic syntheses [7]. The supreme challenge in the selective synthesis of 2-nitroalkanols in the multiple product options such as aldol olefin and its polymer and Cannizzaro products is the selection of an accurate kind of base [8]. Noteworthy developments to the Henry reaction have been realized by means of silyl nitronates in the presence of fluoride ions or instead α-α doubly deprotonated primary nitroalkanes [9]. Both of these processes have shown to be valuable for the stereo selective preparation of vicinal amino alcohols under drastic conditions, which reduces diastereoselectivity with aromatic aldehydes. Hereafter, to find better yields and diastereoselectivity of 2-nitroalcohols, it is essential to advance novel procedures employing heterogeneous catalysts with basic appeal [10].

Heterogeneous catalysis encouraged by solid catalysts such as basic alumina [11] and alumina–KF [12] and homogeneous phase transfer catalysis with surfactants [13] in bi-phase systems are two opposing tactics that were discovered and are intended to attain higher atom selectivity. The solid base catalysts provide an alternative to the classical soluble bases with emphasis on avoiding the environmental problems caused by salt formation and hazardous conditions [14]. Previous work in the synthesis of fine chemicals using layered double hydroxides revealed the importance of such materials and discovered its environmentally favorable routes in comparison to the other catalysts [15–20].

Layered double hydroxide materials (LDHs) have unique features as they represent the basis for new environment-benign technologies concerning inexpensive and highly efficient pathways to catalyze chemical reactions. The general formula of LDHs is $[M^{(II)}_{1-n}\ M^{(III)}_{\ n}(OH)_2]^{n+}\ [(A^{m-}_{n/m}).\ xH_2O]^{n-}$ where A is the interlayer anion with valence m- and negatively charged anions such as NO_3^-, SO_4^{2-}, and CO_3^{2-} encounter the positively charged cationic sheet and the valence "n" is equal to the molar ratio of $M^{III}/(M^{II} + M^{III})$ [18]. The heat treatment of LDHs carried out in the temperature range 400–500 °C leads to a breakdown of the layered structure forming metal oxides mixture. However, the collapsed metal oxide mixture could reform the layered double hydroxide structure after water/anion treatment. LDHs, calcined metal oxide mixtures, or reformed LDH-like structures represent solid base catalysts for different organic reactions in fine chemical production [16–18].

In the present study, MgAl-layered double hydroxide, its calcined form at 500 °C ($MgAlO_x$), and the rehydrated form (MgAl-HT-RH) were synthesized and tested for the Henry reaction between nitroalkanes and different aldehydes. To the author's knowledge, this is the second trial after pioneering work by V. J. Bulbule et al. [21]. However, the present study should be the first extensive study to understand the effect of the mesoporous and basic nature of such catalysts in Henry reactions under the reaction conditions. The obtained promising results could open the gate towards a robust catalyst and a benign process in the Henry reaction.

2. Results and Discussion

2.1. Elemental Chemical Analysis (ICP)

ICP analysis of MgAl-HT was achieved to govern its chemical composition. The analysis discovered that the Mg/Al molar ratio in the solid was 2.8, which is very near to the minimal molar composition of the as-synthesized Mg/Al molar ratio of 3 in the precipitate. This result confirmed the efficacy of the preparation procedure.

2.2. X-ray Diffraction (XRD)

X-ray powder diffraction patterns of the as-synthesized MgAl-HT, thermally treated at 500 °C ($MgAlO_x$), and rehydrated MgAl-HT-RH catalysts are shown in Figure 1. A typical crystalline carbonate containing hydrotalcite phase structure (Ref. Pattern 22-0700, JCPDS) with strong (003), (006), (009), (110), (113) and broadened (015), (018) reflections was observed for the MgAl-HT sample. A crystalline periclase MgO phase was obtained upon thermal treatment of as-synthesized catalyst at 500 °C ($MgAlO_x$) (Ref. Pattern 45-0946, JCPDS) [22]. Thanks to the memory effect, the hydration of the calcined materials using an aqueous alkaline solution of NaOH led to the formation of a layered

double hydroxide-like structure of lower intensity than the original MgAl-HT material. In the present study, we intended to hydrate the calcined material in aqueous alkaline solution to maintain the structure of the layered material and improve its basic nature by introduction of some terminal hydroxyl ions (Brönsted basic sites) [23]. The crystallite size derived from the Scherrer equation [24] showed that MgAl-HT-RH is much lower in size (20 nm) than MgAl-HT (160 nm). The pronounced decrease in the crystallite size of the rehydrated layered double hydroxide structure could improve the catalytic performance towards the Henry reaction.

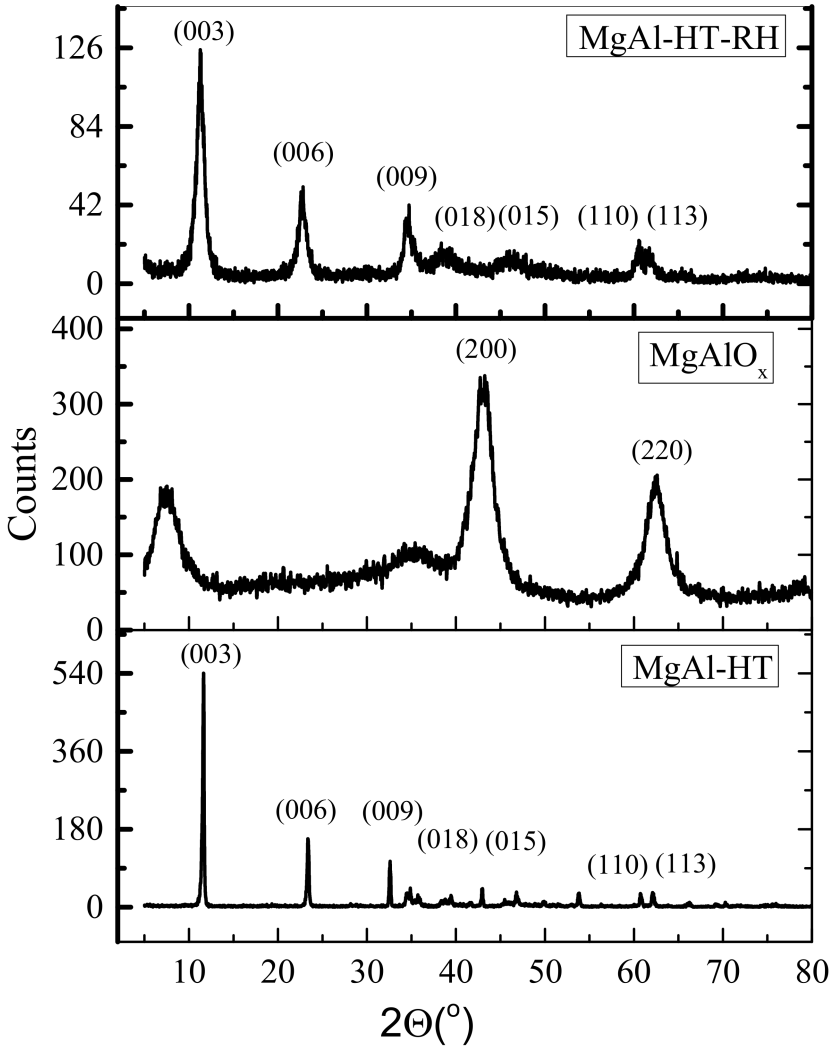


Figure 1. XRD patterns of all the investigated catalysts.

2.3. Scanning Electron Microscopy (SEM)

SEM images of all the investigated catalysts are given in Figure 2. The hydrothermal treatment under autogenous pressure at 170 °C for the coprecipitated MgAl-HT sample (Figure 2A) resulted in the formation of uniform hexagonal platelets of the layered material with 180 nm particle size. The calcination of MgAl-HT led to a pronounced collapse in the layered structure due to the removal of the interlayer anions and thermal decomposition of the hydroxide carbonate into the corresponding metal oxides ($MgAlO_x$) (Figure 2C) [22]. Alkaline treatment of the mixed oxide led to the building of the interlayer gallery between hexagonal platelets of relatively small particle size (20 nm) for MgAl-HT-RH (Figure 2B).

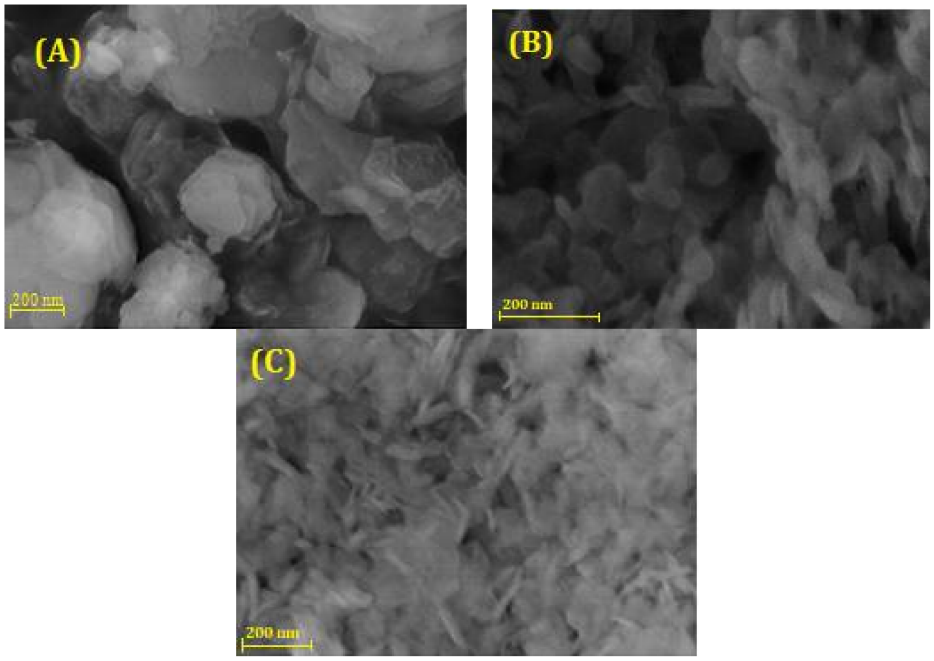


Figure 2. SEM images of: (**A**) MgAl-HT; (**B**) MgAl-HT-RH; (**C**) $MgAlO_x$.

2.4. N_2 Physisorption

N_2 adsorption/desorption isotherms of all the synthesized materials are given in Figure 3. Mesoporous isotherms of Type IV were detected. H3-hysteresis was recorded, which is characteristic of the occurrence of open, relatively large pores that could facilitate reactant/product diffusion through the catalysts [15]. BET surface area of all the investigated solid materials was calculated and is depicted in Table 1. MgAl-HT showed the smallest surface area of all samples (84 m^2/g), while the calcined sample ($MgAlO_x$) recorded the biggest BET surface area (167 m^2/g). The obvious rise in surface area was allocated to the creation of craters through the layers due to development of CO_2 and H_2O [25]. Rehydration of the calcined layered double hydroxide in the alkaline solution by mechanical stirring at room temperature led to an increase in surface area as a result of the breaking of particles and a noticeable exfoliation of the crystals [26].

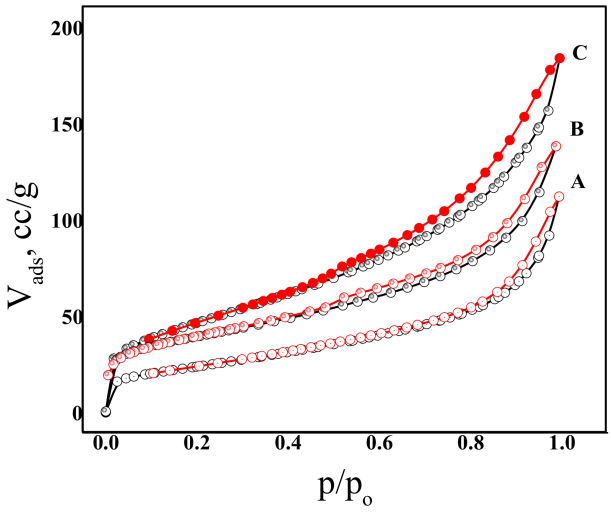


Figure 3. Adsorption-desorption isotherms of all the investigated catalysts; A: MgAl-HT; B: MgAlOx; C: MgAl-HT-RH.

Table 1. BET-surface area, total pore volume and pore radii of all the investigated samples obtained from N_2 adsorption/desorption isotherms.

Sample	S_{BET} (m^2/g)	V_p (cm^3/g)	r_p (Å)	C-Constant
MgAl-HT	84	0.1642	39	177
$MgAlO_x$	167	0.2645	34	86
MgAl-HT-RH	134	0.2014	30	567

2.5. CO_2 Temperature-Programmed Desorption (CO_2-TPD)

The measure of the basicity of the diverse solids was attained by TPD of CO_2. It is well known that types of basic sites can be detected by CO_2 uptake, which is related to diverse types of carbonate coordination in the lamellar interplanetary of layered double hydroxide. The monodentate, bidentate, and bicarbonate anions are often fashioned through the saturation of CO_2 to the basic materials [27]. Monodentate and bidentate carbonate creation contains low-coordination oxygen anions and are then considered as strong basic sites and the creation of bicarbonate anions involves surface hydroxyl groups [28]. The MgAl-HT sample displayed four desorption peaks of relatively low intensity (Figure 4). The low temperature peaks in the range 150–400 °C could be attributed to the desorption of weakly confined CO_2 and breakdown of remaining carbonate ions existing in the MgAl-HT sample [29]. The other two desorption peaks at 450 °C and 665 °C were mostly credited to bicarbonate groups fashioned by the contact of CO_2 with hydroxyl groups in the MgAl-HT and the progress of powerfully attached surface metal carbonate species, respectively. The calcined catalyst ($MgAlO_x$) presented three desorption peaks at 150 °C, 420 °C, and between 510 and 520 °C. The desorption peak at about 420 °C can be accredited to the influence of mostly bidentate carbonate species, together with bicarbonate species. The attendance of a peak at 540 °C is owed to the occurrence of monodentate species. The presence of the two peaks signified the occurrence of OH^- groups with diverse strengths. The differences in CO_2 uptake values between as-synthesized and calcined catalysts can be credited to the presence of misdeeds or linear imperfections in the platelets of the calcined sample. SEM images showed the collapse in the layered structure of hydrotalcite upon thermal treatment at 500 °C. The high intensities of peaks at high temperature could be explained by the formation of Lewis basic sites due to the MgO formation as complemented by XRD data. As we observed, the hydration of the calcined metal oxides (MgAl-HT-RH) resulted in a material with high peak intensity at 420 °C, 500 °C, and a small peak at 620 °C. The pronounced increase in the peak intensity at 420 °C could be attributed to the formation of terminal Brönsted OH^- basic sites together with some Lewis basic sites at high desorption temperature [18]. The pronounced increase in low- and high-temperature basic sites of MgAl-HT-RH could provide superior catalytic activity for this particular catalyst towards solid base catalyzed Henry reactions.

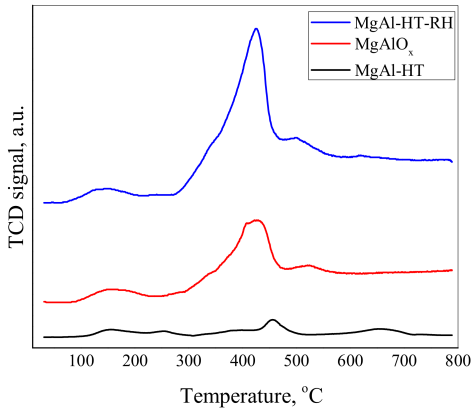
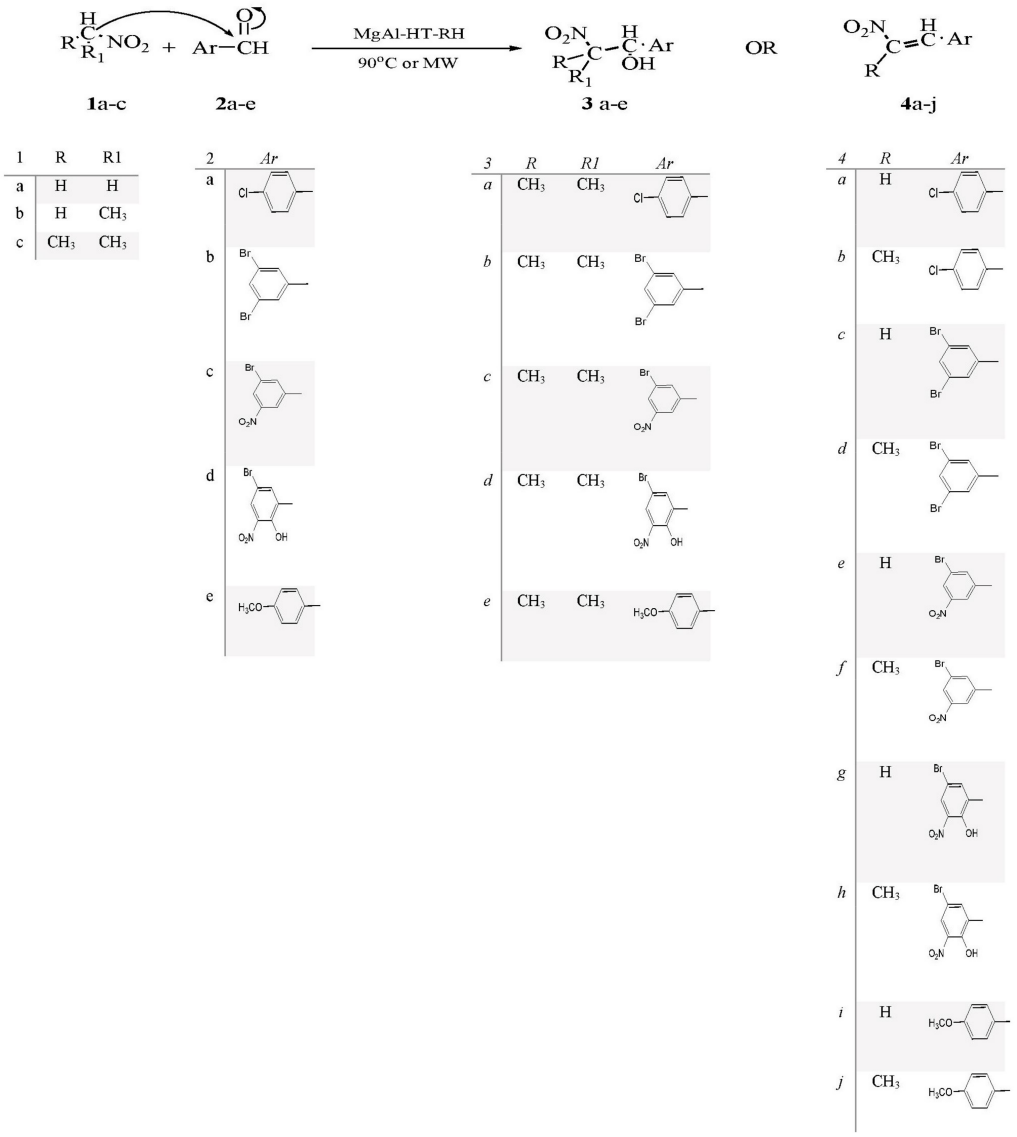


Figure 4. CO_2-TPD profile of all the investigated materials.

2.6. Catalytic Activity Study

The Henry reaction is a base-catalyzed, C–C bond-forming reaction between nitroalkanes and aldehydes or ketones. The catalytic efficacy of MgAl-HT, $MgAlO_x$, and MgAl-HT-RH was tested for the Henry reaction (Scheme 1). The reaction between nitroalkanes (**1a**–**c**) with different aromatic aldehydes (**2a**–**e**) in the presencew of all the catalysts was carried out utilizing conventional methods and solvent-free, microwave-assisted reactions to attain only a single isolable product in each case (as investigated by TLC). The identified products were 2-methyl-2-nitro-1-arylpropan-1-ol derivatives (**3a**–**e**) in the case of 2-nitropropane as a reactant, or 2-nitro-vinylbenzene and 2-nitroprop-1-enylbenzene derivatives (**4a**–**j**) in the cases of nitromethane and nitroethane as reactants, respectively.



1	R	R1
a	H	H
b	H	CH_3
c	CH_3	CH_3

2	*Ar*
a	4-Cl-C$_6$H$_4$
b	2,4-Br$_2$-C$_6$H$_3$
c	2-Br-5-O_2N-C$_6$H$_3$
d	2-Br-3-O_2N-4-OH-C$_6$H$_2$
e	4-H_3CO-C$_6$H$_4$

3	*R*	*R1*	*Ar*
a	CH_3	CH_3	4-Cl-C$_6$H$_4$
b	CH_3	CH_3	2,4-Br$_2$-C$_6$H$_3$
c	CH_3	CH_3	2-Br-5-O_2N-C$_6$H$_3$
d	CH_3	CH_3	2-Br-3-O_2N-4-OH-C$_6$H$_2$
e	CH_3	CH_3	4-H_3CO-C$_6$H$_4$

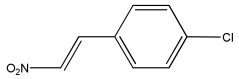
4	*R*	*Ar*
a	H	4-Cl-C$_6$H$_4$
b	CH_3	4-Cl-C$_6$H$_4$
c	H	2,4-Br$_2$-C$_6$H$_3$
d	CH_3	2,4-Br$_2$-C$_6$H$_3$
e	H	2-Br-5-O_2N-C$_6$H$_3$
f	CH_3	2-Br-5-O_2N-C$_6$H$_3$
g	H	2-Br-3-O_2N-4-OH-C$_6$H$_2$
h	CH_3	2-Br-3-O_2N-4-OH-C$_6$H$_2$
i	H	4-H_3CO-C$_6$H$_4$
j	CH_3	4-H_3CO-C$_6$H$_4$

Scheme 1. Reaction of different aldehydes with nitroalkanes utilizing catalyst under different reaction conditions.

All the structures of the isolated products **3a**–**e** and **4a**–**j** were elucidated using IR, ^{1}H NMR, ^{13}C NMR, and MS analyses. The IR showed a characteristic band for OH groups for **3a**–**e** products, which was not recorded for products **4a**–**j**. The mass bands of the isolated products displayed peaks matching their molecular ions.

The catalytic reaction using different investigated catalysts were carried out between **1a** and **2a** under conventional and microwave irradiation and the obtained results are given in Table 2. It is revealed from this table that the MgAl-HT-RH catalyst resulted in satisfactory yields of the products. The reaction carried out under microwave irradiation exhibited improved yield (99%) in a very short reaction time (14 min) in comparison to the conventional conditions (90%, 5 h). Therefore, this specific catalyst was nominated as the greatest catalyst to assess the other reactions and the obtained results are briefed in Figure 5.

Table 2. Catalytic reaction of **1a** with **2a** under conventional and microwave irradiation conditions.

Catalyst	Conventional Method *		Microwave Method **		Product Structure (4a)
	Time (h)	Yield (%)	Time (min.)	Yield (%)	
MgAl-HT	8	61	20	90	
$MgAlO_x$	6	77	18	96	
MgAl-HT-RH	5	90	14	98	

* Reaction conditions: nitromethane (10 mmol), 4-cholorobenzaldehyd (10 mmol), catalyst (0.2 g), 90 °C. ** Reaction conditions: solvent-free conditions, nitromethane (10 mmol), 4-cholorobenzaldehyd (10 mmol), catalyst (0.2 g), MW irradiation (300 W).

It is seen from Figure 5 that MgAl-HT-RH displays an effectual activity and higher % yield in assessment to the reported data [21]. The comparison between this particular catalyst (MgAl-HT-RH) and other heterogeneous catalysts used to catalyze the Henry reaction reported in literature is presented in Table 3. The data obtained from this table revealed that the MgAl-HT-RH catalyst is the best heterogenous catalyst ever used until now for the synthesized Henry products presented in Table 3. The advanced activity of this catalyst is owed to the high surface area (134 m^2/g) and strong Lewis and Brönsted basic sites associated with this catalyst. The hydration of $MgAlO_x$ resulted in the formation of terminal OH^- that increased the basicity of the catalyst [22], accordingly enhancing the catalytic activity of MgAl-HT-RH towards the Henry reaction.

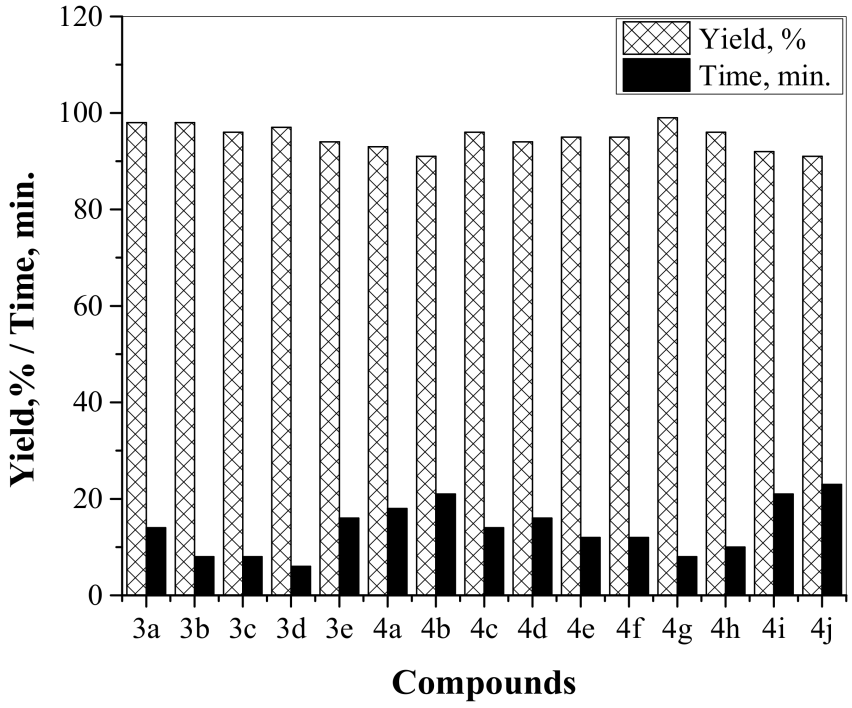


Figure 5. %Yield and reaction time of all the synthesized products utilizing MgAl-HT-RH under microwave irradiation.

Table 3. Henry products over MgAl-HT-RH catalyst and different synthesis routes for the products in the literature.

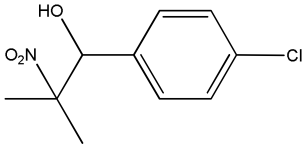
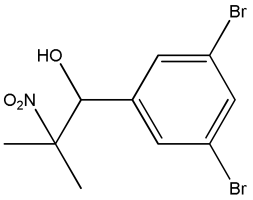
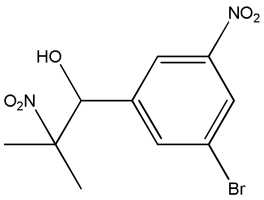
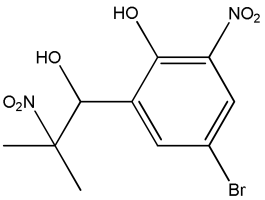
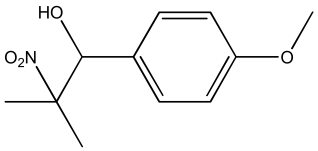
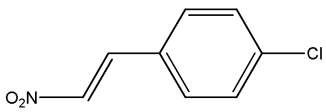
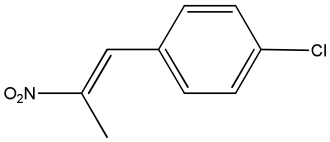
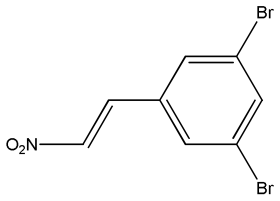
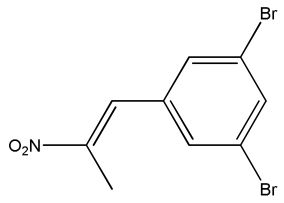
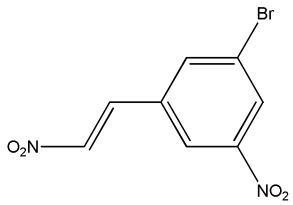
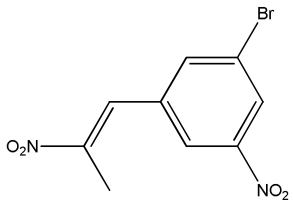
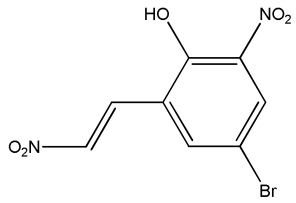
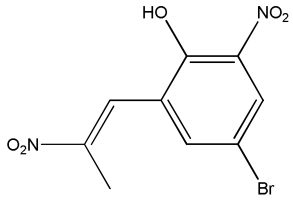
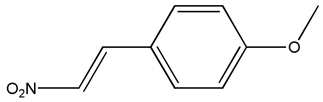
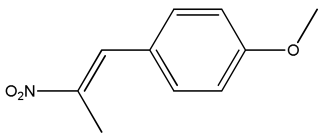
Compound	Reactants	Henry Product Structure	Current Work		Literature Data		
			Yield %	Time min	Yield %	Time h	Ref.
3a	**1c,2a**		95	12	71	11	[30]
3b	**1c,2b**		99	8	-	-	-
3c	**1c,2c**		92	21	-	-	-
3d	**1c,2d**		96	10	-	-	-
3e	**1c,2e**		91	23	68	9	[31]
4a	**1a,2a**		98	14	78	6	[32]
4b	**1b,2a**		93	18	80	6	[33]
4c	**1a,2b**		98	8	75	6	[34]

Table 3. *Cont.*

4d	**1b,2b**		91	21	-	-	-
4e	**1a,2c**		97	6	76	6	[35]
4f	**1b,2c**		94	16	79	7	[36]
4g	**1a,2d**		96	8	-	-	-
4h	**1b,2d**		96	14	-	-	-
4i	**1a,2e**		94	16	68	8	[32]
4j	**1b,2e**		95	12	78	12	[37]

It was vital to study the stability of MgAl-HT-RH catalysts under the microwave operation. Therefore, a particular reaction between **1a** and **2a** was repeated five times with a redeveloped catalyst. The solid catalyst was subsequently filtered and washed by ethanol for each catalytic cycle, then dried in vacuo. The recovered catalyst was tested numerous times (five periods). The catalytic activity was recorded for the time of the achievement of the reaction and the results attained are given in Figure 6.

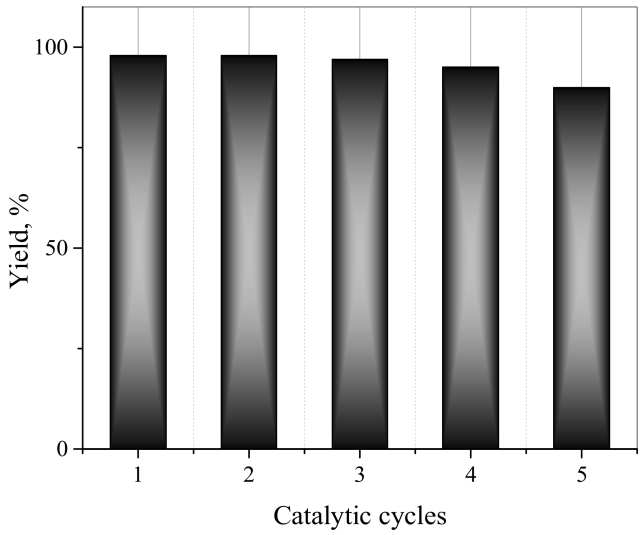


Figure 6. %Yield of **3a** utilizing MgAl-HT-RH for five cycles.

Figure 6 shows that the redeveloped catalyst achieved the reaction capably underneath constant reaction conditions even being subsequently utilized for five times. The observed decay in the catalytic activity was recorded after recycling the catalyst for the fifth time. Our previous studies using XRD technique for the reused catalysts in Aza–Michael addition reactions showed that the reused catalyst was contaminated by organic moieties being adsorbed on the catalyst active sites and caused the temporary poisoning of the regenerated catalyst [15]. The minor deterioration detected in the catalytic action of the MgAl-HT-RH catalyst after reuse for five times could be assigned to the temporary poisoning from organic poisons and/or to the loss in weight by the filtration/washing process.

3. Experimental Section

3.1. Reagents

All chemicals used were of analytical grade purchased from Sigma Alderich (Dorset, UK).

3.2. Catalyst Synthesis

Catalysts were prepared by coprecipitation methods as in the literature [38,39]. Mixing of magnesium nitrate Mg $(NO_3)_2 \cdot 6H_2O$ (0.2213 mol) and aluminium nitrate Al $(NO_3)_3$ (0.0885 mol) in a 0.2213 L of dist. H_2O produced mix (A). Mixing of 0.7162 mol of NaOH and 0. 2084 mol of Na_2CO_3 in a 0.221 L produced mix (B). The steps were as follows: Drop, using a burette, drops from Mix (A) and Mix (B) to a round-bottomed flask 1 L containing 0.5 L distilled water under vigorous stirring and heating at 60 °C and measure pH during precipitation to be 10–11. Keep the temperature at 60 °C overnight (16 h) in water bath. Filter using Whatmann1 filter paper and wash the cake with hot distilled water until pH = 7. Dry the filtrate at 80 °C in an oven for 16 h. The as-synthesized solid was nominated as MgAl-HT. Upon heat treatment, a certain weight of as-synthesized hydrotalcite at 450 °C for 6 h under N_2 atmosphere, a mixture of metal oxide catalyst named $MgAlO_x$ was prepared. Dissolution of $MgAlO_x$ in alkaline solution of 1 M NaOH under vigorous stirring at the room temperature resulted in the creation of layered rehydrated hydrotalcite form nominated as MgAl-HT-RH.

3.3. Catalyst Characterization

The chemical analysis of the prepared solid catalysts was evaluated by using ICP-AES, Optima 7300DV (Perkin Elmmer Corporation, Waltham, MA, USA) apparatus.

X-ray diffraction (XRD) analysis using a Bruker diffractometer (Bruker D8 advance target, Bruker, Karlsruhe, Germany) was utilized using Cu Kα1 and a monochromator (λ = 1.5405 Å) at 40 kV and 40 mA. Particle size of the solid was calculated by means of Scherrer Equation: $D = B\lambda/\beta_{1/2}\cos\theta$, where D is the average particle size of the solid phase under examination, B is the Scherrer constant (0.89), λ is wavelength of the X-ray beam used (1.5405 Å), $\beta_{1/2}$ is the full width at half maximum (FWHM) of the peak, and θ is the angle of diffraction.

A JEOL JSM840A instrument (JEOL, Tokyo, Japan) Scanning Electron Microscope (SEM) was utilized to investigate the morphology of solid samples. Prior to each measurement, the sample was placed on an aluminum block utilizing carbon tape. Physisorption of N_2 at −196 °C using a NOVA 3200e automated gas sorption system (Quantachrome, Boynton Beach, FL, USA) was applied to investigate the pore structure of the solids. Before every measurement, adsorbent was pretreated at 150 °C for 6 h. The Brunauer–Emmett–Teller (BET) equation was applied to determine the specific surface area, while the average pore radius was deduced from the equation: $2V_p/S_{BET}$, as V_p is the total pore volume (at $P/P_0 = 0.98$).

CO_2TPD analysis was performed using CHEMBET 3000 (Quantachrome, FL, USA). Outgassing of the sample at 100 °C (1 h) was performed while passing helium to detach physisorbed water. Then the saturation of the sample with the CO_2 at 120 °C occurred. The temperature-programmed desorption was simply achieved by ramping the adsorbent temperature at 10 °C/min to 800 °C.

3.4. Characterization of Reaction Products

All melting points of the reaction products were measured on a Gallenkamp melting point apparatus and were uncorrected. ^{1}H NMR spectra, ^{13}C NMR spectra were recorded on a Bruker AM250 NMR spectrometer (Bruker, Karlsruhe, Germany) using $CDCl_3$ as solvent for the samples. Mass spectra were recorded on Shimadzu LCMS-QP 800 LC-MS (Kyoto, Kyoto Prefecture, Japan), IR for the synthesized compounds were recorded in potassium bromide discs on a Shimadzu FTIR 8101 PC infrared spectrophotometer. Elemental analysis was obtained using a PerkinElmer 2400 II series CHN Analyser (Waltham, MA, USA). Thin-layer chromatography (TLC) was carried out on precoated Merck silica gel F254 plates. Microwave experiments were carried out using CEM Discover Labmate^{TM} microwave apparatus (300 W with ChemDriver^{TM} Software).

3.5. Typical Procedure for the Catalytic Test Reaction

3.5.1. Method A: Conventional Method

A mixture of aldehydes **2a**–**e** (10 mmol), nitroalkanes **1a**–**c** (10 mmol), and 0.2 g of catalyst were heated together in a three-necked, round-bottomed flask at 90 °C. The progress of the reaction was monitored by TLC. Upon completion of the reaction, the mixture was cooled and the product was extracted by dissolution in hot alcohol. The catalyst was filtered off and washed by alcohol prior to drying and reuse. After evaporation of volatile materials under vacuum, compounds **3a**–**e** and **4a**–**j** were recrystallized from the EtOH/DMF mixture.

3.5.2. Method B: Microwave Irradiation

A mixture of aldehydes **2a**–**e** (10 mmol), nitroalkanes **1a**–**c** (10 mmol), and 0.2 g of catalyst were added in a Teflon vial and irradiated by microwave (300 W) for a required time to complete the reaction (Table 3) in a 2-min interval. The reaction progress was monitored using TLC (eluent; Diethyl ether: chloroform). Then the product mixture was cooled and extracted using ethanol. The catalyst was filtered off and the product compounds were purified by crystallization using an EtOH/DMF solvent mixture to afford the pure crude β-nitroalcoohls **3a**–**e** and the nitrolakenes **4a**–**j** an excellent yield.

Physical and spectral data of the titled compounds 3a–e and 4a–j are listed below (Supplementary Materials).

3a: 1-(4-Chlorophenyl)-2-methyl-2-nitropropan-1-ol.

mp. 192 °C, IR (KBr) υ max/cm^{-1}: 1530 (NO_2), ^{1}H NMR (DMSO): δ 1.1 (s, 3H, CH_3), δ 5.1 (s, H, CH), δ 7.27–7.4 (dd, 4H, ArH's), ^{13}C NMR ($CDCl_3$): δ 25.5, 39.5, 77.82, 81.1 126.66, 130.8, 134.5, MS (*m*/*z*): 230.01 (M^+), Anal. calcd. for $C_{10}H_{12}ClNO_3$ (229), C-52.30; Cl-15.44; H-5.27; N-6.10% Found: C-52.2; Cl-15.44; H-4.01; N-6.8%.

3b: 1-(3,5-Dibromophenyl)-2-methyl-2-nitropropan-1-ol.

mp. above 300 °C, IR (KBr) υ max/cm^{-1}: 3550 (OH), 1523–1550 (NO_2), 670 (C-Br), ^{1}H NMR (DMSO): δ 3.15 (d, 2H, CH_2), 7.27–7.4 (dd, 4H, ArH's), 5.2 (t, 1H, –CH), ^{13}C NMR (CDCl3): δ 25.5, 39.8, 77.8, 88.7, 124.4, 129.8, 131.1, 135.1, MS (*m*/*z*): 353.3 (M^+), Anal. Calcd. for $C_{10}H_{11}Br_2NO_3$ (353), Br-45.27; C-34.02; H-3.14; N-3.97% Found: Br-45.3, C-34.01; H-3.15; N-3.95%.

3c: 1-(3-Bromo-5-nitronitrophenyl)-2-methyl-2-nitropropan-1-ol.

mp. above 300 °C, IR (KBr) υ max/cm^{-1}: 3650 (OH), 1520–1570 ($2NO_2$), ^{1}H NMR (DMSO): δ 1.66 (s, 6H, $2CH_3$), 4.50 (s, H, CH), 7.75–8.29 (m, 3H, ArH's), ^{13}C NMR ($CDCl_3$): δ 16.80, 81.8, 93.0, 122.8, 123.1, 123.7, 139.4, 144.0,149.7 MS (*m*/*z*): 208. (M^+), Anal. calcd. for $C_{10}H_{11}N_2O_5Br$ (328), C-50.00; H-5.04; N-11.66 % Found: C-49.90; H-5; N-11.66%.

3d: 4-Bromo-2-(1-hydroxy-2-methyl-2-nitropropyl)-6-nitrophenol.

mp. above 300 °C, IR (KBr) υ max/cm^{-1}: 3500–3700 (2OH), 1520–1580 ($2NO_2$), 690 (C-Br), ^{1}H NMR (DMSO): δ 1.09, (s, 3H,CH3), 5.2 (s, 1H, –CH), 6.5–7.2 (m, 2H, ArH's), ^{13}C NMR ($CDCl_3$): δ 25.1, 39.48, 88.7, 110.86, 112.36, 117.5, 118.3, 145.3, 147.9, MS (*m*/*z*): 334.9 (M^+), Anal. calcd. for $C_{10}H_{11}BrN_2O_6$ (335), Br-23.84; C-35.9; H-3.3; N-8.4% Found: Br-Br-23.84; C-35.75; H-3.35; N-8.36%.

3e: 1-(4-Methoxyphenyl)-2-methyl-2-nitropropan-1-ol.

mp. above 300 °C, IR (KBr) υ max/cm^{-1}: 3650 (OH), 1535 (NO_2), 1050 (C–O), ^{1}H NMR (DMSO), δ 1.04 (s, 3H, CH_3), 3.14 (s, 3H, CH_3), 5.2 (s, H, CH), 6.9–7.3 (m, 4H, ArH's), ^{13}C NMR ($CDCl_3$): δ 18.02, 44.95, 65.01, 77.8, 84.7, 114.16, 120.86, 129.6, 159.99, MS (*m*/*z*): 225.3 (M^+), Anal. calcd. for $C_{11}H_{15}NO_4$ (225), C-58.66; H-6.71; N-6.22% Found: C-58.66; H-6.71; N-6.22%.

4a: *p*-2-Nitroethenylchlorobenzene.

mp. above 300 °C, IR (KBr) υ max/cm^{-1}: 1515–1560 (NO_2), ^{1}H NMR (DMSO): δ 5.1 (d, 1H, –C=C), 5.6 (d, 1H, –C=C) δ 7.27–7.45 (dd, 4H, Ar), ^{13}C NMR ($CDCl_3$): δ 77.8, 111.22, 127.4, 128.2, 131.8, 134.3, 134.7, MS (*m*/*z*): 183.01 (M^+), Anal. calcd. for $C_8H_6ClNO_2$ (183.6), C-52.61; Cl-19.31; H-3.3; N-7.65% Found: C-52.66; Cl-19.3; H-3.3; N-7.63%.

4b: 1-(*p*-Chlorophenyl)-2-nitro-1-propene.

mp. above 300 °C, IR (KBr) υ max/cm^{-1}: 1525–1570 (NO_2), ^{1}H NMR (DMSO): δ 1.7 (d, 3H, CH_3), 4.9 (q, 1H, –C=CH), 7.2–7.5 (dd, 4H, Ar), ^{13}C NMR ($CDCl_3$): δ 24.5, 77.8, 84.66, 119.8, 128.1, 130, 131.5, 134.7, MS (*m*/*z*): 197 (M^+), Anal. calcd. for $C_9H_8ClNO_2$ (197), C-54.13; Cl-18; H-4.1; N-7% Found: C-50.2; Cl-17.5; H-4. 1; N-6.8%.

4c: 2-Nitroethenyl-3,5-dibromobenzene.

mp. above 300 °C, IR (KBr) υ max/cm^{-1}: 1480 (NO_2), 670 (C-Br), ^{1}H NMR (DMSO): δ δ 5.2 (d, 1H, –C=CH), 6.2 (d, 1H, –C=CH), 7.7–7.9 (m, 3H, ArH's), ^{13}C NMR ($CDCl_3$): δ 77.8, 112.33, 123, 128, 131.1, 135.4, 139.5, MS (*m*/*z*): 307 (M^+), Anal. calcd. for $C_8H_5Br_2NO_2$ (307), Br-57.98; C-31.27; H-1.62; N-4.56% Found: Br-57.7; C-30.57; H-1.6; N-4.46%.

4d: 1-(3,5-Dibromophenyl)-2-nitro-1-propene.

mp. above 300 °C, IR (KBr) υ max/cm^{-1}: 1545 (NO_2), 672 (C-Br), ^{1}H NMR (DMSO): δ 1.7 (d, 3H,CH_3) 5.9 (q, 1H, –C=CH), 7.7–7.9 (m, 3H, ArH's), ^{13}C NMR ($CDCl_3$): δ 24.9, 77.8, 119.7, 123, 128.77, 130, 131.7, 139.4 MS (*m*/*z*): 321.9 (M^+), Anal. calcd. for $C_9H_9Br_2NO_3$ (322), Br-49.8; C-34; H-2.2; N-4.4% Found: Br-49.79; C-33.68; H-2.20; N-4.36%.

4e: 2-(2-Nitroethenyl)-4-bromo-6-nitrophenol.

mp. above 300 °C, IR (KBr) υ max/cm^{-1}: 3600 (OH), 1520–1580 ($2NO_2$), 675 (C-Br), ^{1}H NMR (DMSO): δ 5.1 (d, 1H, C=CH), 5.63 (H, OH), 6.1(d, 1H, C=CH), 6.9–7.2 (dd, 2H, ArH's), ^{13}C NMR ($CDCl_3$): δ 77.8, 112.3, 113, 115, 120, 126, 130, 135.8, 138.5, MS (*m*/*z*): 289 (M^+), Anal. calcd. for $C_8H_5Br_2NO_2$ (289), Br-27.64; C-33.24; H-1.74; N-9.69% Found: Br-27.64; C-33.24; H-1.74; N-9.69%.

4f: 2-[-2-Nitro-1-propenyl]-4-bromo-6-nitrophenol.

mp. above 300 °C, IR (KBr) υ max/cm^{-1}: 3650 (OH), 1540 ($2NO_2$), 675 (C-Br), ^{1}H NMR (DMSO): δ 1.75(d, 3H, CH_3), 4.95 (q, H, C=CH), 5.6 (s, H, OH), 6.9–7.2 (dd, 2H, ArH's), ^{13}C NMR ($CDCl_3$): δ 24.82, 77.82, 114, 115.86, 119, 120, 126, 13.5, 136.1, 138.9, MS (*m*/*z*): 302 (M^+), Anal. calcd. for $C_9H_7BrN_2O_5$ (303), Br-26.37; C-35.67; H-2.33; N-9.24% Found: Br-26.37; C-35.67; H-2.33; N-9.24%.

4g: 4-bromo-2-Nitro-6-(2-nitovinyl) phenol.

mp. 232 °C, IR (KBr) υ max/cm^{-1}: 1510–1555 ($2NO_2$), ^{1}H NMR (DMSO): δ 7.29 (d, H, C=H), 7.36 (d, H, C=H), 7.68,8.07 (2, 2H, ArH's), ^{13}C NMR ($CDCl_3$): δ 117.5, 121.7, 122.2, 131.6, 133.9, 134.9, 135.5, 150.1, MS (*m*/*z*): 298 (M^+), Anal. calcd. for $C_8H_5N_2O_5Br$ (298), C-32.21; H-1.67; N-9.39% Found: C-32.42; H-1.53; N-8.94%.

4h: 4-bromo-2-Nitro-6-(2-nitroprop-1-enyl) phenol.

mp. 229 °C, IR (KBr) υ max/cm^{-1}: 1515–1560 ($2NO_2$), ^{1}H NMR (DMSO): δ 1.75, (s, 3H, CH3), 7.14 (s, 1H, C=CH), 7.69,2.07 (2s, 2H, ArH's), ^{13}C NMR ($CDCl_3$): δ 16.9, 116.5, 119.7, 127.5, 127.6, 137.4, 137.7, 141.0, 149 MS (*m*/*z*): 307.5 (M^+), Anal. calcd. for $C_9H_7N_2O_5Br$ (312), C-34.62; H-2.24; N-8.97% Found: C-34.93; H-2.12; N-8.46%.

4i: *p*-[-2-Nitroethenyl]methoxybenzene.

mp. 266 °C, IR (KBr) υ max/cm^{-1}: 1545 (NO_2), 1150 (C–O), ^{1}H NMR (DMSO): δ 3.15 (s, H, CH_3), 5.2 (d, 1H, –C=CH), 6.1 (d, 1H, C=CH), 7–7.4 (m, 4H, ArH's), ^{13}C NMR ($CDCl_3$): δ 65.5, 77.8, 113, 127.7, 128.66, 135.4, 156.5, MS (*m*/*z*): 179 (M^+), Anal. calcd. for $C_9H_9NO_3$ (197), C-60.33; H-5.06; N-7.82% Found: C-60.33; H-5.06; N-7.82%.

4j: 1-(*p*-Methoxyphenyl)-2-nitro-1-propene.

mp. above 300 °C, IR (KBr) υ max/cm^{-1}: 1565 (NO_2), 1210 (C–O), ^{1}H NMR (DMSO): δ 1.75 (d, 3H, CH_3), 3.14 (s, 3H, CH_3), 4.9 (m, 1H, –C=CH), 7–7.4 (m, 4H, ArH's), ^{13}C NMR ($CDCl_3$): δ 24, 77.8, 84.7, 112.86, 119.83, 127.7, 128.5, 130.33, 156.79, MS (*m*/*z*): 193.1 (M^+), Anal. calcd. for $C_{10}H_{11}NO_3$ (193), C-56.86; H-6.20; N-6.63 % Found: C-56.86; H-6.20; N-6.63%.

4. Conclusions

In brief, solid base catalysts from the layered double hydroxide family, MgAl-HT, its calcined mixture ($MgAlO_x$), and activated alkali-treated oxide mixture (MgAl-HT-RH) were successfully synthesized and fully characterized using different techniques. The Henry reaction between benzaldehyde and nitromethane over solid base catalysts was attained. MgAl-HT-RH catalyst gave a precious advantage over all other solid base catalysts utilizing conventional or microwave-assisted reaction conditions. The microwave irradiation technique introduced high yields of β-alcohol derivatives using the layered double hydroxide catalysts in a very short time. Novel Henry products

were synthesized in good yield (96%) in the current work for the first time. The relatively large surface area, mesoporous nature, and strong basic sites of rehydrated catalyst (MgAl-HT-RH) were responsible for the power of catalytic activity. The catalyst was reusable and its activity could be sustained after five catalytic cycles. The catalysts' superior efficiency and sustainability for carbon–carbon coupling via the Henry reaction makes them a promising candidate for further coupling reactions.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/8/4/133/s1, Figure S1: Spectral data of compounds **3a**–**e** and **4a**–**j**.

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Conflicts of Interest: The authors declare no conflict of interest.

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