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 re-hydrated one at 25°C (MgAl-HT-RH) were synthesized. Physicochemical properties of the catalysts were characterized by x-ray diffraction (XRD), scanning electron microscopy (SEM). Surface area of the as-synthesized, calcined and re-hydrated catalysts was determined by N_2 physisorption at -196°C. CO_2-teperature 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 re-hydrated solid catalyst were responsible for their superior catalytic efficiency. The robust nature was determined by using the same catalyst for five times, where the product % yield was almost unchanged significantly.

Key words: C-C bond formation, Henry reaction; Solid base catalyst; Layered double hydroxide

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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 Henry reaction using soluble bases such as alkali metal hydroxides, carbonates, bicarbonates, alkoxides, alkaline earth metal hydroxide, and 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 produce 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 to be recovered the catalyst from the products. In the last decade, there were notable improvements in the development of heterogeneous catalyst for Henry reaction [6].

The extraordinary growth in the struggle in the industry has pushed the researchers to advance more effective catalytic processes in the synthesis of fine chemicals. The products of the Henry reaction, that representing C–C bond formation, are significant materials widely used in numerous 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 Cannizaro products is the selection of the accurate kind of base [8]. Noteworthy developments to the Henry

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reaction have been achieved by using silyl nitronates in the existence of fluoride ion or instead α- α doubly deprotonated primary nitroalkanes [9]. Both of these processes have showed to be valuable for the stereo selective preparation of vicinal amino alcohols under drastic conditions, which reduced diastereoselectivity with aromatic aldehydes. Hence to obtain better yields and diastereoselectivity of 2-nitroalcohols, it was necessary to develop new procedures employing heterogeneous catalysts with basic character.

Heterogeneous catalysis induced by solid catalysts such as basic alumina [11], alumina–KF [12] and homogeneous phase transfer catalysis with surfactants [13] in bi-phase system, the two divergent approaches being explored are aimed at achieving higher atom selectivity. The solid base catalysts provide an alternative to the classical soluble bases with emphasize to avoid the environmental problems caused by salt formation and hazardous conditions [14]. Previous wok 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].

In the present study MgAl-layered double hydroxide, its calcined form at 500^{o}C (MgAlO$_x$) and the re-hydrated form (MgAl-HT-RH) were synthesized and tested for 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 mesoporous and basic nature of such catalysts in Henry reaction under the reaction conditions. The obtained promising results could open the gate towards a robust catalyst and a benign process in 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 500ºC ($MgAlO_x$) and re-hydrated MgAl-HT-RH catalysts are shown in Fig. 1. A typical crystalline carbonate containing hydrotalcite phase structure (Ref. Pattern 22-0700, JCPDS) with strong (003), (006), (009), (110) and (113) and broadened (015) and (018) reflections was observed for MgAl-HT sample. A crystalline periclase MgO phase was obtained upon thermal treatment of as-synthesized catalyst at 500ºC ($MgAlO_x$) (Ref. Pattern 45-0946, JCPDS) [22]. Thanks to the memory effect the hydration of the calcined materials using aqueous alkaline solution of NaOH led to the formation of 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 is aqueous alkaline solution to maintain the structure of layered material and improve its basic nature by introduction of some terminal hydroxyl ions (BrÖnsted basic sites) [23]. The crystallite size derived from Scherrer equation [24] showed that Mg-Al-HT-RH is much lower in size (20 nm) than MgAl-HT (160 nm). The pronounced decrease in the crystallite size of the re-hydrated layered double hydroxide structure could improve the catalytic performance towards Henry reaction.

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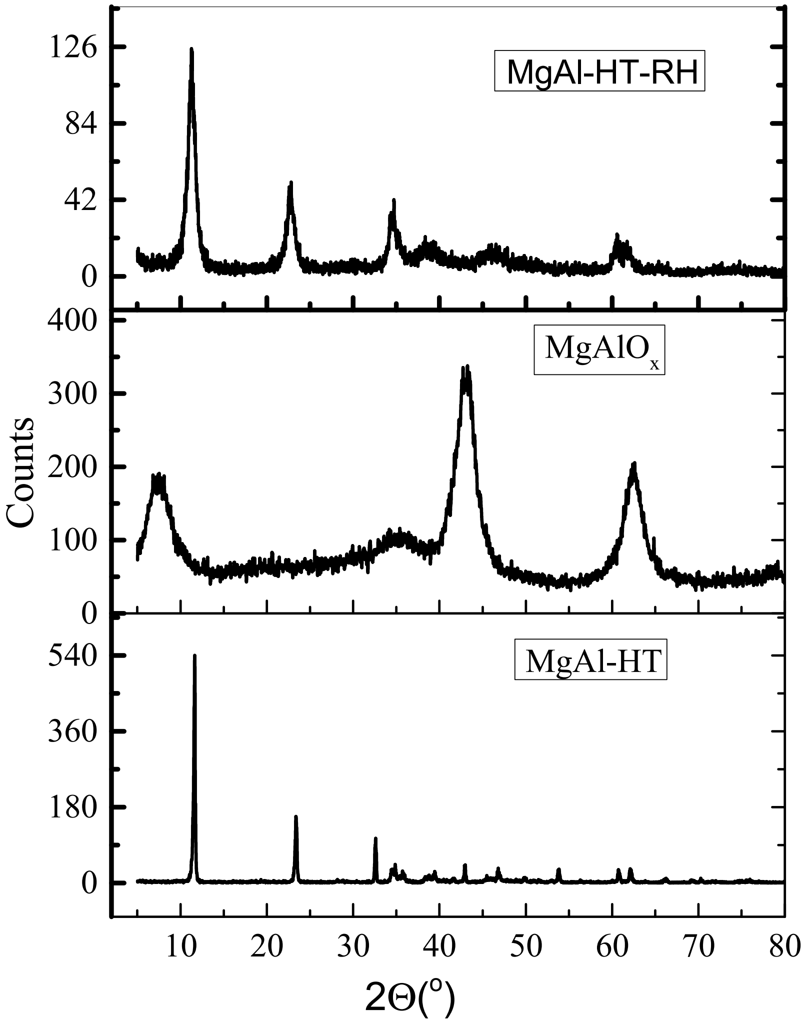

Figure 1. XRD patterns of all the investigated catalysts.

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 (Fig. 2: A) 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

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anions and thermal decomposition of the hydroxide carbonate into the corresponding metal oxides ($MgAlO_x$) (Fig. 2:C) [22]. Alkaline treatment of the mixed oxide led to build the interlayer gallery between hexagonal platelets of relatively small particle size (20nm) for MgAl-HT-RH (Fig. 2: B).

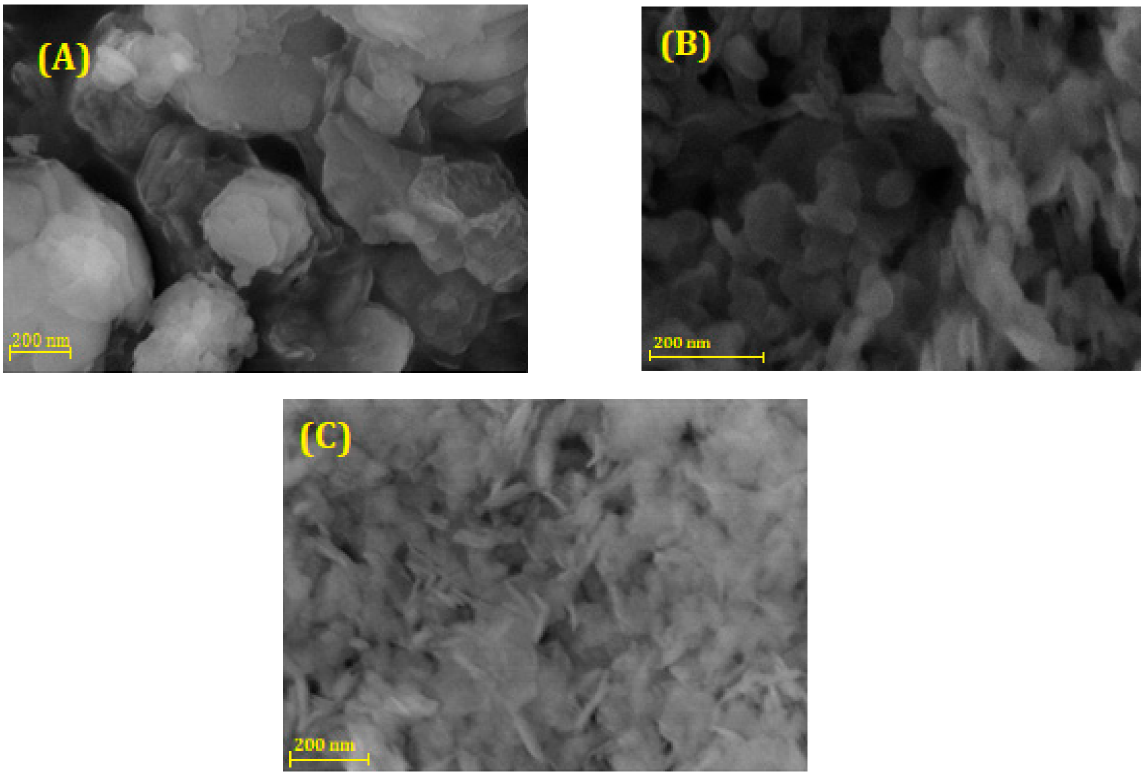

Figure 2. SEM images of: (A) MgAl-HT; (B) MgAl-HT-RH; (C) $MgAlO_x$

2.4 N_2 Physisorption

N_2 adsorption/desorption isotherms of all the synthesized materials are given in Fig. 3. Mesoporous isotherms of Type IV were detected. H3-hysteresis was recorded, which is characteristic for the occurrence of open relatively large pores that could facilitate reactants/products diffusion through the catalysts [15]. BET-surface area of all the investigated solid materials was calculated and depicted in Table 1. MgAl-HT showed the smallest surface area of all samples (84 m^2/g), while the calcined

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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]. Re-hydration 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 break of particles and a noticeable exfoliation of the crystals [26].

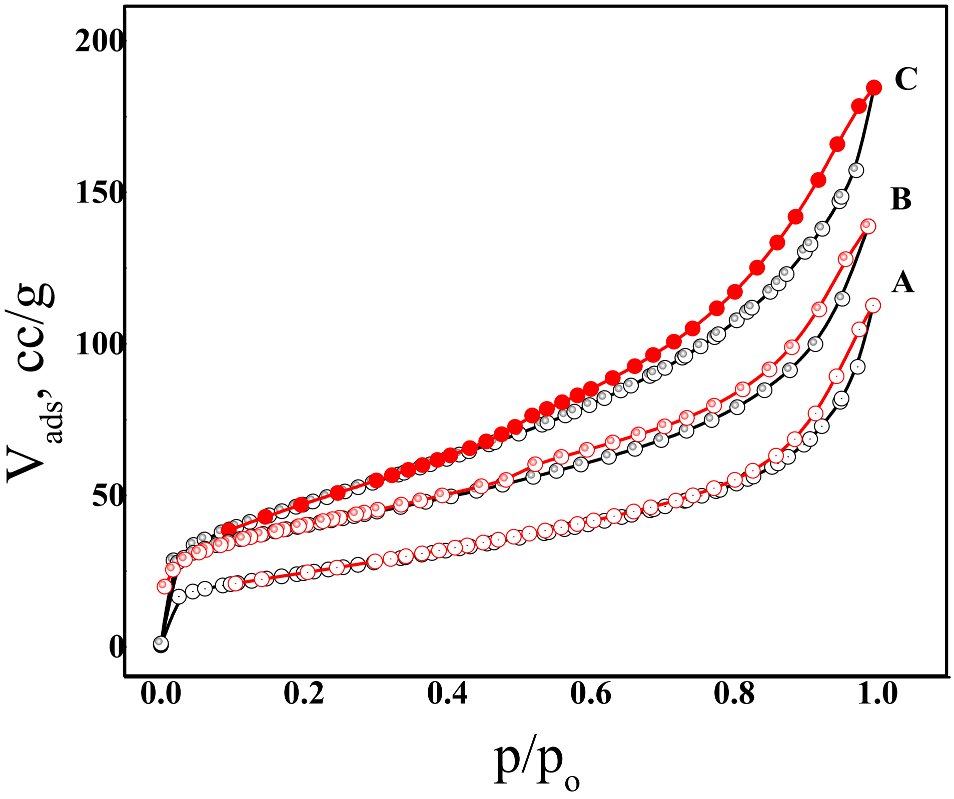

Figure 3. Adsorption-desorption isotherms of all the investigated catalysts; A: MgAl-HT; B: MgAlOx; C: MgAl-HT-RH

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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 different solids was attained by TPD of CO_2. It is well known that types of basic sites could be detected by CO_2 uptake, which is related to different types of carbonate coordination in the interlayer space of layered double hydroxide. The mono-dentate, bi-dentate and bicarbonate anions often fashioned through the saturation of CO_2 to the basic materials [27]. Mono-dentate and bi-dentate carbonate creation contains low-coordination oxygen anions and are therefore 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. The low temperature peaks in the range 150°C- 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 was mostly credited to bicarbonate groups fashioned by the interaction of CO_2 with hydroxyl groups in the MgAl-HT

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and the development of strongly attached surface metal carbonate species, respectively. The calcined catalyst ($MgAlO_x$) presented three desorption peaks at 150ºC, 420ºC and between 510 and 520ºC. The desorption peak at about 420˚C can be accredited to the influence of mostly bi-dentate carbonates species, together with bicarbonate species. The attendance of a peak at 540˚C is owed to the occurrence of mono-dentate species. The presence of the two peaks suggesting the presence of OH^- groups with different strength. The differences in CO_2 uptake values between as-synthesized and calcined catalysts can be attributed to the existence of irregularities or linear defects in the platelets of the calcined sample. SEM images showed the collapse in the layered structure of hydrotalcite upon thermal treatment at 500ºC. 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 420ºC, 500ºC and small peak at 620ºC. The pronounced increase in the peak intensity at 420ºC 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 reaction.

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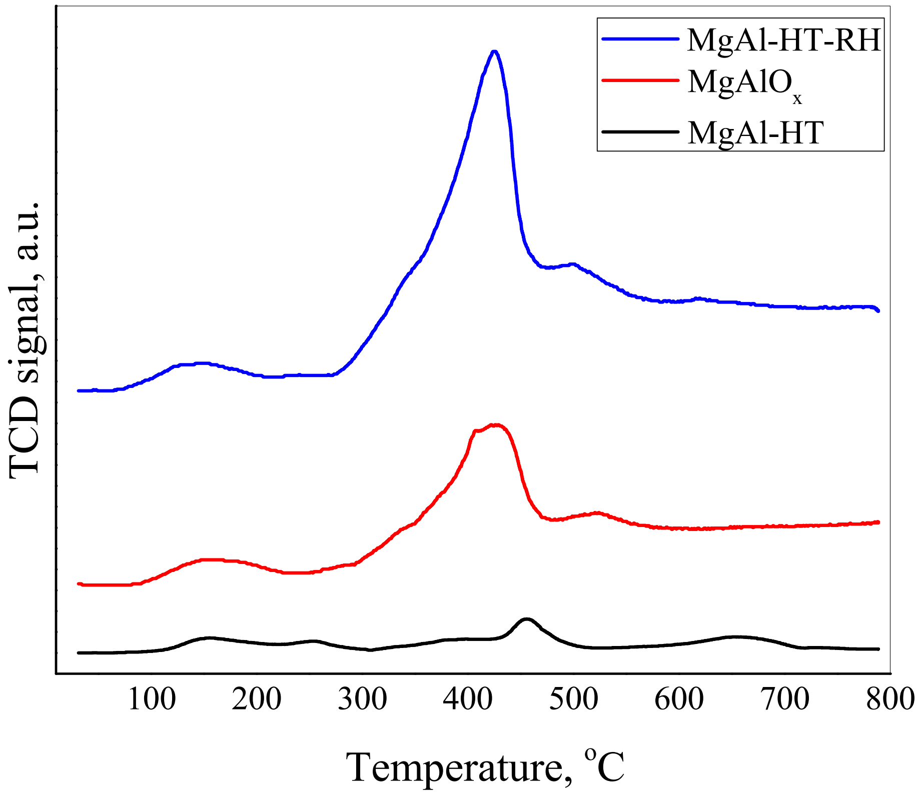
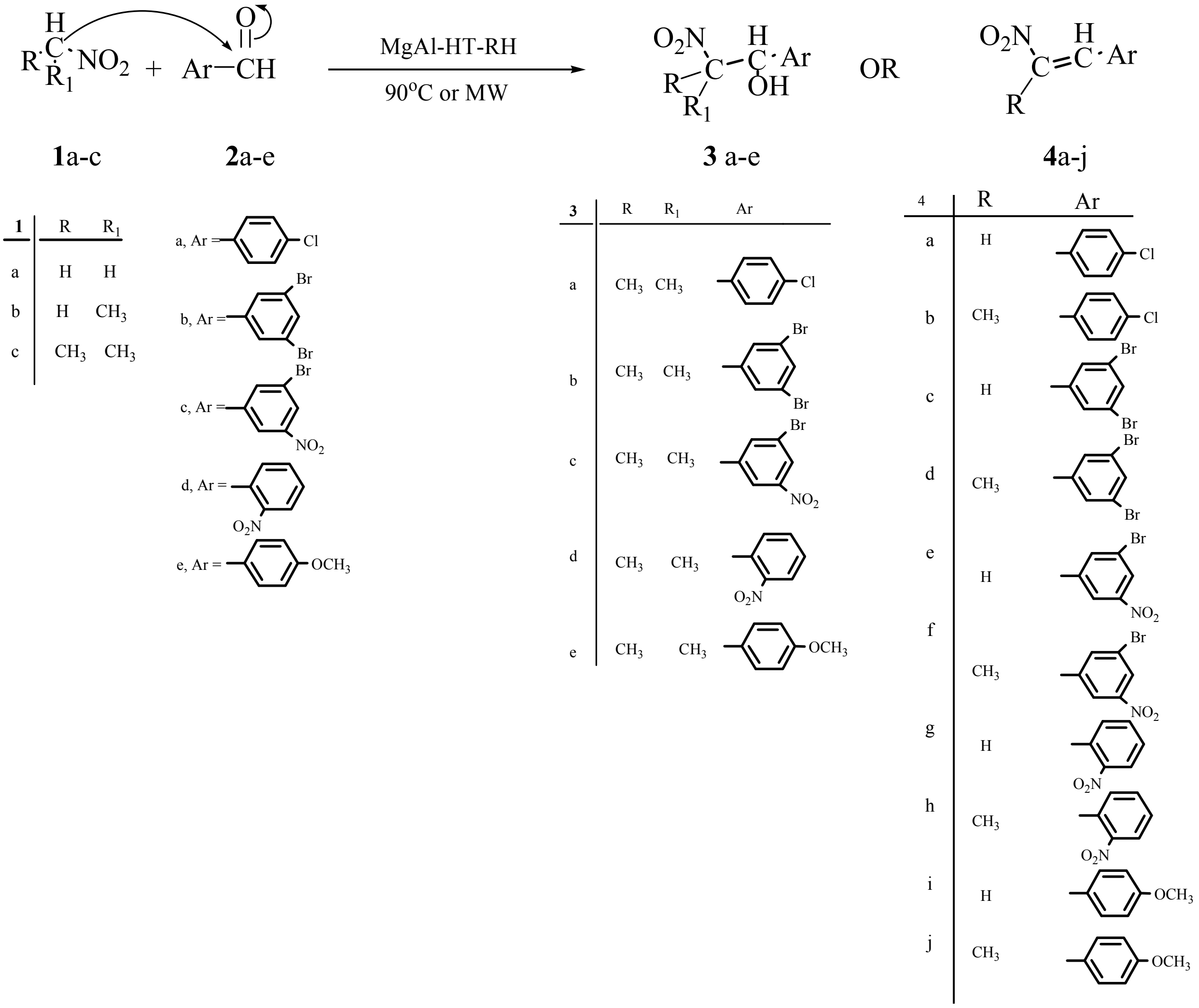


Figure 4. CO_2-TPD profile of all the investigated materials

2.6 Catalytic activity study

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 were tested for Henry reaction (Scheme1). The reaction between nitroalkanes (**1a-c**) with different aromatic aldehydes (**2a-e**) in the existence of all the catalysts was carried out utilizing conventional method and solvent free microwave assisted reaction, to obtain only one isolable product is each case, (as investigated by TLC). The identified products were 2-methyl-2-nitro-1-arylpropan-1-ol derivatives (**3a-e**) in case of 2-nitropropane as a reactant or 2-nitro-vinylbenzene and 2-nitroprop-1-enylbenzene derivatives (**4a-j**) in case of nitromethane and nitroethane as reactants, respectively.



Scheme I

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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 group for **3a-e** products, which was not recorded for products (**4a-j**). The mass spectra of the isolated products showed peaks corresponding to 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 form this table that MgAl-HT-RH catalyst resulted in satisfactory yields of the products. The reaction carried out under microwave irradiation showed better yield (99%) in a very short reaction time (14 min.) in comparison to the conventional conditions (90%,5h). Therefore, this specific catalyst was nominated as the best catalyst to test the other reactions and the obtained results are summarized in Fig. 4.

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

Catalyst	Conventional method *		Microwave method **	
	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

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*Reaction conditions: nitromethane (10mmol), 4-cholorobenzaldehyd (10mmol), catalyst (0.2 g), 90°C.

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

It is seen from Fig.4 that MgAl-HT-RH displays an effectual activity and higher % yield in comparison to the literature data [21]. The higher activity of this catalyst is due 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 enhances the catalytic activity of MgAl-HT-RH towards Henry reaction.

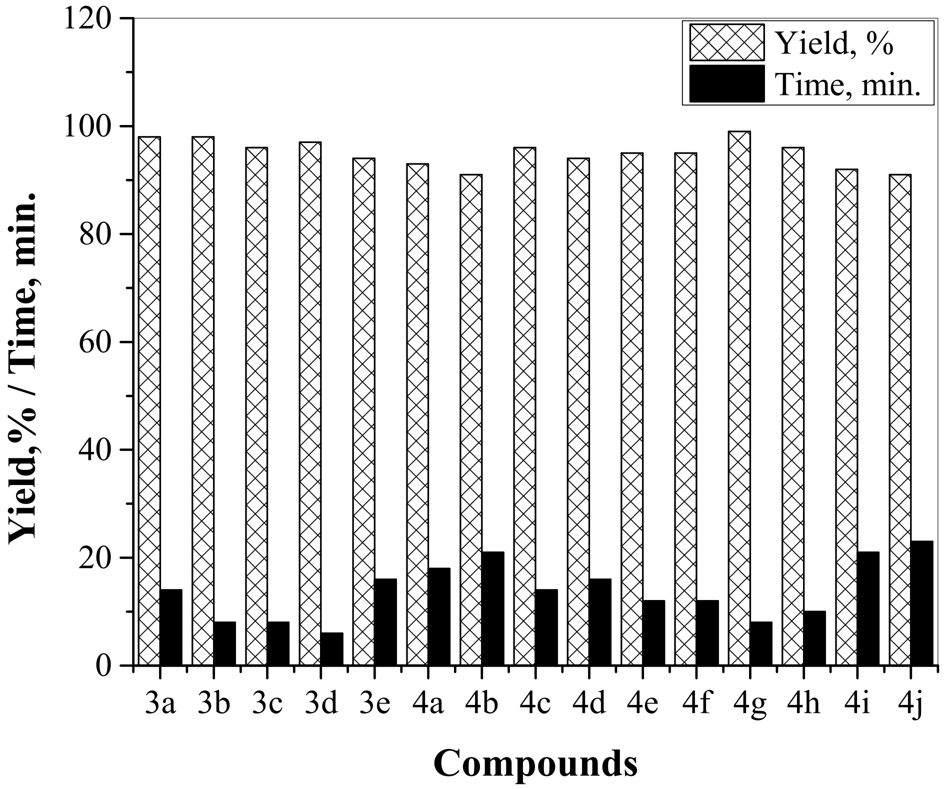

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Figure 4. %Yield and reaction time of all the synthesized products utilizing MgAl-HT-RH under microwave irradiation.

It was essential to study the robust of MgAl-HT-RH catalysts in the microwave assisted reactions. Consequently, a selected reaction between **1a** and **2a** was repeated five times using a regenerated catalyst. The catalyst was filtered and washed after each catalytic cycle with ethanol and dried under vacuo. The recovered catalyst is reused several times (five times) and the time required to accomplish the reaction was taken as an indication of catalytic activity and the results obtained are given in Figure 6.

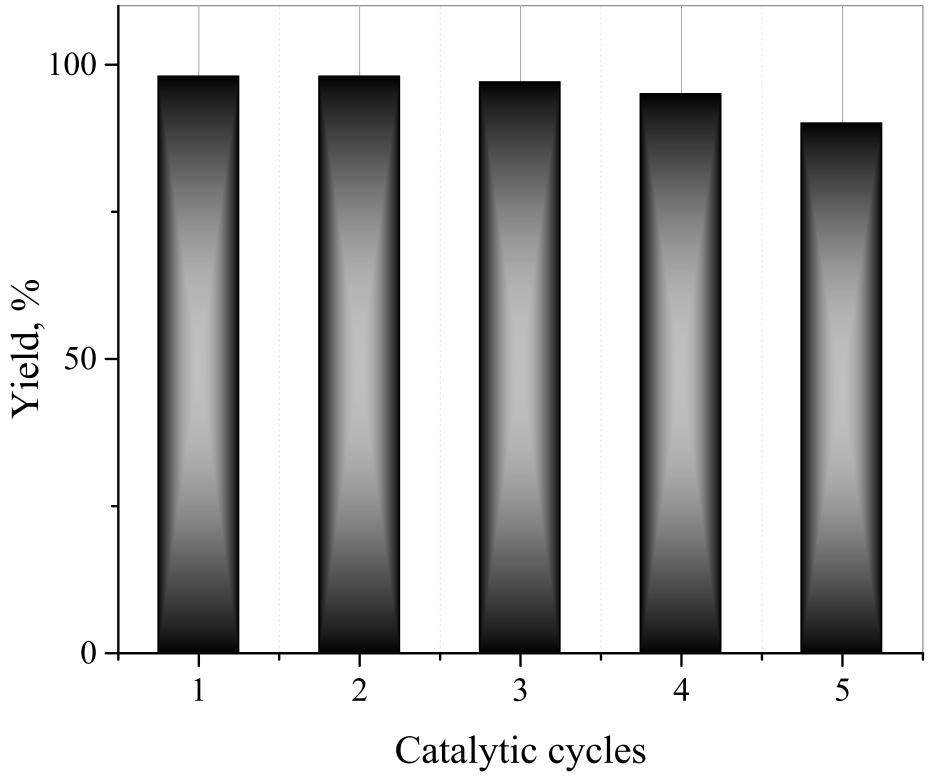

Figure 6. %Yield of **3a** utilizing MgAl-HT-RH for five cycles

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Fig. 6 shows that the regenerated catalyst performs the reaction efficiently under constant reaction conditions even after being used for five times. The slight decay observed in catalytic activity of MgAl-HT-RH catalyst on the fifth time of being used could be attributed to temporary poisoning of organic contaminants and/or to the loss in weight by filtration/washing process [15].

3. Experimental Section

3.1 Reagents

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

3.2 catalyst synthesis

Catalysts were prepared by co-precipitation methods as literature [29-30]. Mixing of magnesium nitrate Mg $(NO_3)_2.6H_2O$ (0.2213 mol), and aluminium nitrate Al $(NO_3)_3$ (0.0885 mol), in a 0.2213 L of dist. H_2O, mix (A). Mixing of 0.7162 mol of NaOH, and 0. 2084 mol of Na_2CO_3, in a 0.221 L, mix (B). Drop using a burette drops from Mix (A) and Mix (B) to a round bottomed flask 1L containing 0.5 L distilled water under vigorous stirring and heating at 60ºC and measure pH during precipitation to be 10-11. Keep the temperature at 60ºC overnight (16 h) in water bath. Filter using (Whatmann1 filter paper) and washing the cake by hot distilled water till pH =7. Dry the filtrate at 80 ^{0}C in an oven for 16 h. The as-synthesized solid nominated as

MgAl-HT. Upon heat treatment a certain weight of as-synthesized hydrotalcite at 450oC 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 room temperature led to the formation of layered rehydrated hydrotalcite form nominated as MgAl-HT-RH.

3.3Catalyst characterization

The elemental composition of the synthesized materials was determined by using ICP-AES, Optima 7300DV (Perkin Elmmer Corporation, Waltham, MA, USA) instrument. The sample preparation for elemental analysis was carried out as follows: approximately 100 mg of material was placed in a Teflon beaker and the material was dissolved in a mixture of acids (10 mL of 40% HF, 4 mL of HNO_3 and 4 mL HCl) and then 20 mL of deionized H_2O was added to the solution. The solution was then kept in an ultrasonic bath for 10 min to obtain homogeneous dissolution. Then, the solution was transferred into a centrifuge tube and centrifuged at 3000 rpm for five minutes. The clear supernatant solution was decanted and used to prepare 250 mL stock solution.

Powder X-ray diffraction (XRD) measurements were carried out using a Bruker diffractometer (Bruker D8 advance target) (Bruker, Karlsruhe, Germany). The patterns were obtained using Cu Kα1 and a monochromator ($\lambda = 1.5405$Å) at 40 kV and 40 mA. The crystallite size of the catalysts phase was calculated using Scherrer

Equation: $D = B\lambda/\beta_{1/2} \cos\Theta$, where D is the average crystallite size of the phase under investigation, 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 diffraction peak and Θ is the diffraction angle. The identification of different crystalline phases in the samples was performed by comparing the data with the Joint Committee for Powder Diffraction Standards (JCPDS) files.

Scanning Electron Microscopy (SEM) measurements were carried out using a JEOL JSM840A instrument (JEOL, Tokyo, Japan). For measurements, the powder sample was attached to an aluminum block using double sided carbon tape. The textural properties of the synthesized samples were determined from the N_2 physisorption measurements at -196°C using a NOVA 3200e automated gas sorption system (Quantachrome, Boynton Beach, FL, USA). Prior to measurement, the sample was outgassed for 6 h at 150°C. The specific surface area was determined by using the Brunauer-Emmett-Teller (BET) equation. The average pore radius was estimated from the relation $2V_p/S_{BET}$, where V_p is the total pore volume (at P/P_0 = 0.975).

CO_2TPD analysis was performed using CHEMBET 3000 (Quantachrome, Florida, USA). Samples were degassed at 100°C for one hour in flowing helium to remove water vapor. Next the sample is saturated with the CO_2 at 120°C. The

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temperature-programmed desorption is easily performed by ramping the sample temperature at 10°C/minute 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 are uncorrected. ^{1}H-NMR spectra, ^{13}C-NMR spectra were recorded on Bruker AM250 NMR spectrometer using $CDCl_3$ as solvent for the samples. Mass spectra were recorded on Shimadzu LCMS-QP 800 LC-MS, IR for the synthesised compounds were recorded in potassium bromide discs on Shimadzu FTIR 8101 PC infrared spectrophotometer. Elemental analysis was obtained using PerkinElmer 2400 II series CHN Analyser. Thin-layer chromatography (TLC) was carried out on pre-coated 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** (10mmol) and 0.2 g of catalyst were heated together in a three-necked round bottomed flak at 90^{o}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 re-use. After

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evaporation of volatile materials under vacuum, compounds **3a-e** and **4a-j** were re-crystallized from EtOH/DMF mixture.

3.5.2 Method B: microwave irradiation

A mixture of aldehydes **2a-e** (10 mmol), nitroalkanes **1a-c** (10mmol) and 0.2 g of catalyst were added in a Teflon vial and irradiated by microwave (300W) for a required time to complete the reaction (Table 3) in a 2 minutes 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 EtOH/DMF solvent mixture to afford the pure crude β-nitroalcoohls **3a-e** and the nitrolakenes **4a-j** in an excellent yield.

Physical and spectral data of the titled compounds **3a-e** and **4a-j** are listed below

3a: 1-(4-chlorophenyl)-2-methyl-2-nitropropan-1-ol ($C_{10}H_{12}ClNO_3$)

mp. 192°C, IR (KBr) ʋ 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 $C_{10}H_{11}Br_2NO_3$

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mp. above 300ºC, IR (KBr) ʋ 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: 4-bromo-2-(1-hydroxy-2-methyl-2-nitropropyl)-6-nitrophenol

mp. above 300ºC, IR (KBr) ʋ 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%.

3d: 2-methyl-2-nitro-1-(2-nitrophenyl)propan-1-ol

mp. above 300ºC, IR (KBr) ʋ max/cm^{-1}: 3650 (OH), 1520-1570 ($2NO_2$), ^{1}H NMR (DMSO): δ 1.04 (s, 3H, CH_3), 5.15 (s, H, CH), 6.7–7.2 (m, 4H, ArH's), ^{13}C NMR ($CDCl_3$): δ 25.12, 39.9, 77.82, 88.65, 112.86, 116.75, 129.36, 150.99, MS (m/z): 208. (M^+), Anal. Calcd for $C_{10}H_{12}N_2O_5$ (240), C-50.00; H-5.04; N-11.66 % Found: C- 49.90; H-5; N-11.66 %.

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

mp. above 300ºC, IR (KBr) ʋ 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,

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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 ($C_8H_6ClNO_2$)

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 ($C_9H_8ClNO_2$)

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: 1-(3,5-Dibromophenyl)-2-nitro-1-propene ($C_9H_7Br_2NO_2$)

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.

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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; %

4d: 2-Nitroethenyl-3,5-dibromobenzene $C_8H_5Br_2NO_2$

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): 306.5 (M^+), Anal. Calcd for $C_8H_5Br_2NO_2$ (307), Br-52; C-31.5; H-1.7; N-4.58% Found: Br-51.7; C-30.57; H-1.6; N-4.46 %.

4e: 2-(2-Nitroethenyl)-4-bromo-6-nitrophenol ($C_8H_5BrN_2O_5$)

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 ($C_9H_7BrNO_2$)

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%.

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4g: *o*-[-2-Nitroethenyl]nitrobenzene, $C_8H_6N_2O_4$

mp. 232°C, IR (KBr) υ max/cm^{-1}: 1510-1555 ($2NO_2$), ^{1}H NMR (DMSO): δ 5.2 (d, H, C=H), 6.1 (d, H, C=H), 6.8 – 7.4 (m, 4H, ArH's), ^{13}C NMR ($CDCl_3$): δ 77.8, 110.9, 112.87, 115.4, 120.6, 125.6, 127.2, 135.4, 149.1, MS (m/z): 194 (M^+), Anal. Calcd for $C_8H_6N_2O_4$ (194), C-49.49; H-3.12; N-14.43% Found: C-49.49; H-3.12; N-14.43%.

4h: 2-Nitro-1-(*o*-nitrophenyl)-1-propene $C_9H_8N_2O_4$

mp. 229°C, IR (KBr) υ max/cm^{-1}: 1515-1560 ($2NO_2$), ^{1}H NMR (DMSO): δ 1.75, (d, 3H, CH3), 4.9 (q, 1H, C=CH), 6.8–7.3 (m, 4H, ArH's), ^{13}C NMR ($CDCl_3$): δ 24.6, 77.8, 111.6, 115.57, 121, 126, 127.8, 130.3, 149.1, MS (m/z): 307.5 (M^+), Anal. Calcd for $C_9H_8N_2O_4$ (308), C-51.93; H-3.87; N-13.46% Found: C-51.93; H-3.87; N-13.46%.

4i: *p*-[-2-Nitroethenyl]methoxybenzene $C_9H_9NO_3$

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 $C_{10}H_{11}NO_3$

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mp. above 300ºC, IR (KBr) υ max/cm^{-1}: 1565 (NO_2), 1210 (C-O), ^1H 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 %.

Conclusions

In brief, we reported Henry reaction between benzaldehyde and nitromethane over solid base catalysts. MgAl-HT-RH catalyst gave a precious advantage over all other solid base catalysts utilizing conventional or microwave assisted reaction conditions. Microwave irradiation technique introduced high yields of β- alcohol derivatives using the layered double hydroxide catalysts in very short time. 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.

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Conflict of interest

The authors declare that, there is no conflict of interest

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