# Mg–V/CO<sub>3</sub> hydrotalcite: an efficient and reusable catalyst for one-pot synthesis of multisubstituted pyridines

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**Abstract** Mg–V/CO<sub>3</sub> hydrotalicite (Mg–V/CO<sub>3</sub> HTlc) as an effective heterogeneous catalyst was synthesized by a simple technique. The catalyst was identified by PXRD, TEM, SEM and BET surface area analysis. The catalyst is fully recyclable and reusable for several runs preserving its high activity. The catalytic activity of Mg–V/CO<sub>3</sub> HTlc is described by synthesis of a series of pyridines in good to excellent yields via a facile one-pot multicomponent reaction with a shorter reaction time.

**Keywords** Heterogeneous catalyst  $\cdot$  Multicomponent reaction  $\cdot$  Mg–V/CO<sub>3</sub> HTlc  $\cdot$  Pyridines  $\cdot$  Reusability  $\cdot$  One-pot synthesis

# Introduction

Pyridine-based heterocyclics form a major cluster in organic synthesis [1]. They are constituents of many natural products and pharmaceuticals, which exhibit a wide range of biological activity [2–4]. Within a long-term research program aimed at developing pharmaceutically active materials, synthesss of substituted pyridines are of special importance because of their varied biological activities [5], such as anticancer [6], antimicrobial [7], antibacterial [8], antifungal [9], anti-inflammatory [10], and antioxidant activity [11], cytotoxicity [12] and anti-HIV [13]. Thus, the synthesis of poly substituted pyridine derivatives has fascinated many researchers, and several approaches have been pursued using catalysts such as MgO [14], LaMnO<sub>3</sub>

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[15], [bmIm]Br [16], [bmIm]OH [17], BF<sub>3</sub>/MCM-41 [18], K<sub>5</sub>CoW<sub>12</sub>O<sub>40</sub>·3H<sub>2</sub>O [19] and Co/SiO<sub>2</sub> [20].

In recent years, multicomponent reactions (MCRs) have been developed as a powerful strategy in the synthesis of organic [21], agro- [22], combinatorial [23], bioactive medicinal [24] and heterocyclic molecules [25]. Advantages of MCRs are wide, including simple protocols, inexpensive reactants and green principles. One-pot MCRs are often feasible with shorter reaction times, while affording higher chemical yields than multiple-step syntheses, resulting in conservation of energy and manpower. Thus, such environmentally benign protocols are opportune and much desired.

In this context, heterogeneous catalysts with potential for recyclability and reusability have great scope and will be attractive in one-pot reactions involving MCRs. For such a role, hydrotalcites and hydrotalcite-like compounds (HTlcs) are good candidates which have proven records as catalysts and supports, and as ion-exchangers. Thermal calcination of these compounds at 450 °C leads to the formation of highly basic mixed metallic oxides with moderate surface area which are potential catalysts for various base-catalyzed condensation reactions [26]. Relative to conventional linear syntheses, this eco-friendly quick protocol has benefits such as cost-effectiveness, atom economy and scope to engineer the surface properties.

In continuation of our research work in the domains of MCRs [27–30], we recently reported the synthesis procedure for dihydropyridines, using acetanilide, ammonium hydroxide and aromatic aldehydes in the presence of water at 60 °C and using Zn–V/CO<sub>3</sub> hydrotalcite as the catalyst with good yields [31]. Based on that success, in this communication we report another reaction for multisubstituted pyridines involving acetanilide, malononitrile and 11 different aldehydes, using ethanol as solvent, Mg–V/CO<sub>3</sub> hydrotalcite as catalyst and the reaction occurring at room temperature with further improved yields. We believe that this is the first report of the use of a heterogenous catalyst to promote a fast MCR protocol for the synthesis of multisubstituted pyridines at RT with eco-friendly ethanol as solvent (Scheme 1).

#### Experimental

All chemicals and reagents required for the reaction were of analytical grade and were used without any further purification. Melting points were determined in open

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Scheme 1 Synthesis of multifunctional pyridines (3a-k)

capillaries on a Mel-Temp apparatus and are uncorrected. A Bruker AMX 400 MHz NMR spectrometer was used to record the <sup>1</sup>H NMR, <sup>13</sup>C NMR and <sup>15</sup>N NMR (400 MHz) spectral values. The CDCl<sub>3</sub>/DMSO- $d_6$  solution was utilized for this while TMS served as the internal standard. TMS was further used as an internal standard for reporting all the chemical shifts in  $\delta$  (ppm). The FT-IR spectrum for the samples was established using a Perkin Elmer Precisely 100 FT-IR spectrometer at the 400–4,000 cm<sup>-1</sup> area. LCMS spectral data was recorded on a MASPEC low resolution mass spectrometer operated at 70 eV. The purity of all the reaction products was confirmed by TLC using aluminum plates coated with silica gel (Merck Kieselgel 60 F254).

Preparation of catalyst

The double-layered hydroxide Mg–V/CO<sub>3</sub> HTlc with a molar ratio of 2.0:1.6:0.4 was prepared by adapting the co-precipitation method described elsewhere [31] using a constant pH. A mixed metal solution of magnesium and vanadium nitrates with preferred concentrations was prepared and 0.30 M sodium hydroxide and 0.20 M sodium carbonate were added concurrently to a 500-ml beaker at the rate of 50 ml/h, with constant stirring at RT, at a pH of 11–12.5. The precipitate formation occurred at 12 h at 65 °C, and the precipitate was separated immediately by filtration. Next, the precipitate was washed repeatedly with deionized water to remove the free nitrate ions. The precipitate was dried gradually at 100 °C over 12 h to afford the Mg–V/CO<sub>3</sub> HTlcs. This was further calcined at 450 °C for 4 h.

Characterization of catalysts

A Micromeritics Tristar-II porosity and surface area analyzer was used for estimation of the pore size, pore volume and surface area of the catalysts. BJH adsorption–desorption curves were obtained at -196 °C to assess the particulate properties of the catalyst. All the catalyst materials were degassed by passing nitrogen overnight at 200 °C. A Bruker D8 advance instrument with a Cu K radiation source by  $\lambda = 1.5406$  was used for the X-ray diffraction data for the catalyst.

A Jeol JEM-1010 electron microscope and JEOL JSM-6100 microscope were used for TEM and SEM analysis, respectively. In TEM analysis for particles distribution, the size of 40–60 particles were averaged with standard deviation. An emission current (100  $\mu$ A) by a Tungsten (W) filament with 12 kV accelerator voltage was employed for EDX-analysis of the SEM images. Elemental composition of the catalyst materials was established by using an inductively coupled plasma optical emission spectrometer (Optima 5300 DV).

General procedure for the synthesis of pyridines

A mixture of acetoacetanilide (1 mmol), benzaldehyde (1 mmol), and malononitrile (1 mmol) were dissolved in ethanol (10 ml) and added to the Mg–V/CO<sub>3</sub> HTlc (20 mg) catalyst at RT and stirred continuously for 45 min. TLC was performed to observe the complete consumption of the starting material in the reaction mixture. A

crude product was afforded upon filtering the reaction mass and subsequent evaporation under reduced pressure. This crude was then recrystallized by an EtOAc:Hexane mixture to obtain the pure product (3a-k). The filtered catalyst was washed with ethanol and dried, being reused for six successive runs.

### **Results and discussion**

With the aim of maximizing the yield and reducing reaction times, in order to establish the optimum reaction conditions, the reaction was investigated out under varied conditions of catalysts and solvents. In a pilot experiment, acetoacetanilide (1), benzaldehyde (2a), and malononitrile were conducted in ethanol without any catalyst at room temperature (RT), but with no reaction. Even after 48 h under reflux conditions, no reaction was able to obtain any product (Table 1, entries 1 and 2). A trace amount of the anticipated product was achieved when  $K_2CO_3$  and NaOH were used as catalysts in the ethanol media (Table 1, entries 3 and 4), but no reaction was observed in the presence of strongly basic catalysts, such as Cs/Al<sub>2</sub>O<sub>3</sub>

	+ $CHO$ Catalyst CH <sub>3</sub> $CH_2(CN)_2$ 2a $C_2H_5OH, 45 min,$	N N H H <sub>3</sub> C N O CN CN CN CN CN CN CN CN CN CN	
Entry	Catalyst	Solvent	Yield (%) <sup>a</sup>
1	No catalyst	EtOH	No reaction
2 <sup>b</sup>	No catalyst	EtOH	No reaction
3	K <sub>2</sub> CO <sub>3</sub>	EtOH	08
4	NaOH	EtOH	12
5	Cs/Al <sub>2</sub> O <sub>3</sub>	EtOH	No reaction
6	V/Al <sub>2</sub> O <sub>3</sub>	EtOH	No reaction
7	MgO	EtOH	37
8	Mg–Al HTlc	EtOH	48
9	Mg–V/CO <sub>3</sub> HTlc Uncal	EtOH	54
10	Mg–V/CO <sub>3</sub> HTlc	EtOH	94
11	Mg-V/CO <sub>3</sub> HTlc	THF	80
12	Mg-V/CO <sub>3</sub> HTlc	CH <sub>3</sub> CN	78
13	Mg–V/CO <sub>3</sub> HTlc	DCM	85
14	Mg-V/CO <sub>3</sub> HTlc	DMF	82

Table 1	Optimization	condition	for the	synthesis	of pyridines	by	Mg-V/C	03	HTlc
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All products were characterized by NMR and mass spectral analysis

<sup>a</sup> Isolated yields

<sup>b</sup> Under reflux for up to 48 h

and V/Al<sub>2</sub>O<sub>3</sub> with the ethanol solvent (Table 1, entries 5 and 6). With MgO, simple HTlc (Mg-Al) and uncalcined Mg-V/CO<sub>3</sub> HTlc as catalysts in ethanol, 37, 48 and 54 % yields were obtained, respectively (Table 1, entries 7 and 8). Next, we tried to synthesize the heterocyclic framework using Mg-V/CO<sub>3</sub> HTlc as the catalyst with ethanol as the solvent. To our delight, in just 45 min at RT, a multicomponent reaction was accomplished successfully and produced the expected substituted pyridine (3a) selectively and in good yield (94 %) (Table 1, entry 10). The identity of the product was confirmed by spectral and analytical data (ESI). The HTlc catalysed reaction was found to proceed almost instantaneously, although about 45 min was taken for completion of the reaction. In the proposed MCR, Mg-V/CO<sub>3</sub> HTlc displayed greater efficiency compared to the other catalysts investigated due to the synergetic effect of the metal. Normally, the basic nature of hydrotalcite is the crucial factor in its catalytic activity. The surface properties of HTlcs can be modified by loading the cations of varied properties. Inclusion of  $V^{3+}$  into HTlc in place of  $Al^{3+}$  provides acidity and acidic sites on the catalyst surface. An optimal distribution of the acidic and basic sites due to loading of Mg-V/CO<sub>3</sub> mixed oxides possibly contributed to its enhanced catalytic efficiency, which is evident from the high yield, selectivity and speed of the reaction achieved in the title reaction.

Taking advantage of the proven performance of Mg–V/CO<sub>3</sub> as the catalyst for the MCR, we then focused on simplifying the protocol for the reaction. Firstly, we performed screening tests varying the HTlc used. Results of the effect of Mg–V/CO<sub>3</sub> HTlc concentration on the reaction yields of **3a** were also presented (see ESI). With the amount of Mg–V/CO<sub>3</sub> HTlc increased from 10 mg to 20 mg, the yield increased from 75 to 94 % (Table S1, entry 2). However, further enhancement in the amount of catalyst had only a marginal effect on product yield (ESI, Table S1, entry 1). Furthermore, the ethanol as solvent (Table 1, entry 10) displayed superiority to the other solvents examined THF (Table 1, entry 11), CH<sub>3</sub>CN (Table 1, entry 12), DCM (Table 1, entry 13) and DMF (Table 1, entry 14).

The scope of the catalyzed MCR was further explored. Choosing the optimal conditions for the synthesis of **3a**, i.e. 20 mg of Mg–V/CO<sub>3</sub> HTlc at RT and ethanol as solvent (Scheme 1), we employed variious structurally different aldehydes (**1b**–**k**) for the MCR. To our delight, most of the reactions afforded the desired pyridine derivatives (**3b–k**) in good yields (82–94 %) with good selectivity and with no by-products. The results are depicted in Table 2. The MCRs with substrates bearing electron-donating or electron-withdrawing groups on the aromatic ring proceeded smoothly and formed the corresponding multisubstituted pyridines (**3a–k**) was established and confirmed on the basis of elemental analysis and spectral data [<sup>1</sup>H NMR, <sup>13</sup>C NMR, <sup>15</sup>N NMR (GHSQC) and mass]. The details of the product characterization are presented in the ESI.

Powder X-ray diffractogram (XRD)

The sample crystallinity was examined using PXRD analysis. The PXRD pattern of calcined MgVCO<sub>3</sub> HTlc is shown in Fig. 1. The diffractogram of the catalyst is in

CH <sub>N</sub> H 1	Ar – CHO ( $2a$ -k) CH <sub>2</sub> (CN) <sub>2</sub> Mg-V/CO <sub>3</sub> HTlc C <sub>2</sub> H <sub>5</sub> OH, 45 min, rt	$ \begin{array}{c}                                     $	
Entry	Ar ( <b>2a–l</b> )	Product	Yield (%) <sup>a</sup>
1 <sup>b</sup>	C6H5 (2a)	3a	No reaction
2	2a	3a	94
3	2-OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ( <b>2b</b> )	3b	92
4	$4\text{-OCH}_{3}C_{6}H_{4}$ (2c)	3c	90
5	2-ClC <sub>6</sub> H <sub>4</sub> ( <b>2d</b> )	3d	92
6	$2-NO_2C_6H_4$ (2e)	3e	89
7	$4-BrC_{6}H_{4}$ ( <b>2f</b> )	3f	90
8	4-N(CH <sub>3</sub> )2C <sub>6</sub> H <sub>4</sub> (2g)	3g	91
9	$2\text{-BrC}_{6}\text{H}_{4}$ (2h)	3h	90
10	Furyl (2i)	3i	92
11	4-FC <sub>6</sub> H <sub>4</sub> ( <b>2j</b> )	3ј	92
12	$4-CF_{3}C_{6}H_{4}(2\mathbf{k})$	3k	93

Table 2 Synthesis of multisubstituted pyridines by Mg-V/CO<sub>3</sub> HTlc (3a-k)

All products were characterized by NMR and mass spectral analysis

<sup>a</sup> Isolated yields

<sup>b</sup> Without catalyst



**Fig. 1** XRD spectra of Mg–V/ CO<sub>3</sub> hydrotalcite

good agreement in the standard hydrotalcite peaks, the indexes of which correlate with the reported hydrotalcites [32]. The value of the calculated c-axis corresponds to three times the thickness of the 'sandwich' formed between the two consecutive brucite-like structures and the interlayer where carbonate ions exist together. The thickness calculated from the position of the diffraction peak corresponding to the

(0 0 3) plane was recorded in the range of 7.3–7.6 Å for carbonate precursors. Other main peaks corresponding to the plane (0 0 6) were recorded in the range of 3.5–3.8 Å for carbonate precursors. The two sharp intense peaks at low diffraction angles of 23.2° and 26.9° are ascribed to the diffraction by basal planes (006) and (102) [33]. Furthermore, broad, less intense peaks at higher angles around 31.4, 36.5, 41.4, 45.8 and 60° and indexed to (105), (108), (110), (113) and (200) planes also confirm the carbonate-containing hydrotalcite structure [34]. Powder diffractorate tograms and the *d*-spacing values of mixed metal oxide precursors for MgVCO<sub>3</sub> correlate with the ICDD file No. 50-532.

# SEM, TEM and ICP-OES analysis

The SEM micrograph (Fig. 2) shows that agglomeration of the metal oxide particles, which is caused by the calcination of the HTlc precursor and these aggregates, range from 0.85 to 2.00  $\mu$ m. EDS analysis of this catalyst showed that Mg and V are homogenously distributed in the catalyst, and the metal ratio (Mg:V) is also in agreement with the ICP elemental analysis. The catalyst morphologies as indicated by the SEM image clearly indicate the homogeneity in shape for the sample and the high crystallinity. ICP–OES analysis showed that the magnesium to vanadium metal ratio is 1:3 which a stoichiometric metal ratio of the hydrotalcite. The TEM micrograph in Fig. 3 shows that the calcined catalyst has a cubic-like structure, which is a typical vanadate structure. Thes sixe of these cubic planar structures is  $24 \pm 3$  nm. The selected area diffractions showed that the catalyst is polycrystalline in nature which is further observed by the XRD-diffractogram.

# Surface area analysis

The  $N_2$  isotherms of type-IV with a  $H_2$  hysteresis loop were used for the catalyst sample (Fig. 4) [35]. This was symptomatic of their mesoporous structure. A quite



Fig. 2 SEM spectra of Mg–V/CO<sub>3</sub> hydrotalcite



Fig. 3 TEM spectra of Mg-V/CO<sub>3</sub> hydrotalcite



Fig. 4 N2 adsorption and desorption spectra and pore size distribution of Mg-V/CO3 HTlc

narrow and mono-modal pore size distribution was obtained for the MgV-doped carbonate mesoporous HTlcs. The relative pressure  $(P/P_0)$  range of 0.3–0.7 of the hysteresis loops indicates the fairly small pore size and good homogeneity of the catalyst [36]. This further indicated that the average pore size was increased with increasing the loading amount of the carbonate with a specific surface area (16.2 m<sup>2</sup>/g), pore size (0.014 cm<sup>3</sup>/g) and total pore volume (71 Å). The large surface areas were obtained for the catalyst sample with high pore volumes due to the narrow pore size distribution of the catalyst.



Fig. 5 Recyclability of Mg-V/CO<sub>3</sub> hydrotalcite catalyst

Reusability of Mg-V/CO3 HTlcs

The facile heterogeneous character of the catalyst was shown by a recycling experiment using the model reaction. After completion of the reaction, the catalyst was recovered by filtration, washed with ethanol and dried under vacuum. The recovered catalyst was reused for six times with a slight loss in catalytic activity (Fig. 5). The minor loss observed in the catalytic activity after the 6th run could be due to temporary poisoning by organic impurities or due to minor changes in the structure and morphology of the catalyst under the operating conditions.

# Conclusion

In conclusion, we report an efficient and environmentally benign one-pot multicomponent protocol for the synthesis of multisubstituted pyridines with good atom efficacy. We have developed a simple, highly efficient and recyclable heterogeneous catalyst, Mg–V/CO<sub>3</sub> HTlc, for MCR protocol at RT, which can be put into practice for the selective synthesis of multisubstituted pyridines using eco-friendly ethanol. The main objectives of mild reaction conditions, use of a recyclable catalyst, costeffectiveness and an eco-friendly simple method are achieved.

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