Clean synthesis of benzylidenemalononitrile by Knoevenagel condensation of benzaldehyde and malononitrile: effect of combustion fuel on activity and selectivity of Ti-hydrotalcite and Zn-hydrotalcite catalysts

AMARSINH L JADHAV and GANAPATI D YADAV*

Departmental of Chemical Engineering, Institute of Chemical Technology, Nathalal Parekh Marg, Matunga, Mumbai, Maharashtra 400 019, India

E-mail: gdyadav@yahoo.com; gd.yadav@ictmumbai.edu.in

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Abstract. Benzylidene malononitrile find applications in pharmaceutical industries, pharmacology, biotech, specialty chemicals, perfumery, and for fluorescence-based assay to determine methane and is produced by polluting routes. Hydrotalcites (HT) have been very effective as solid bases in different reactions and their properties can be changed by using different synthetic methods. In this work, the effect of additional metal in the synthesis of Al-Mg hydrotalcite was systematically studied to prepare Ti-Al-Mg (Ti modified hydrotalcite) and Zn-Al-Mg HT (Zn modified hydrotalcite) using combustion method with glycine as well as glycerol as a fuel. All synthesized catalysts were evaluated in Knoevenagel condensation of benzaldehyde with malononitrile to give benzylidene malononitrile. The catalysts were completely characterized by SEM, EDXS, N₂ Adsorption, CO₂-TPD and NH₃-TPD and XRD techniques. Ti-Al-Mg hydrotalcite using glycine as a fuel was found to be the most active, selective and reusable catalyst. Langmuir-Hinshelwood-Hougen-Watson (LHHW) model was used to establish the reaction mechanism and kinetics. All species were weakly adsorbed leading to the second order power law model. Using mole ratio of 1:3 of benzaldehyde to malononitrile with ethyl acetate as a solvent and 2.5×10^{-4} g/cm³ catalyst loading, 67.1% conversion of benzaldehyde and 97.6% selectivity to benzylidene malononitrile were achieved in 4 h at 60 °C. The apparent activation energy was 10.01 kcal/mol. The process is green.

Keywords. Combustion synthesis; hydrotalcite; Ti-Al-Mg hydrotalcite; Knoevenagel condensation; benzylidene malononitrile (or 2-benzylidenepropanedinitrile).

Nomenclature

A	reactant species A, benzaldehyde	C _E	concentration of E, product species (mol/cm ³)
B	reactant species B, malononitrile	C _{ES1}	concentration of E on active sites of type S ₁ (mol/g)
C _A	concentration of A, benzaldehyde (mol/cm ³)	C _{S1}	concentration of vacant sites of type S ₁ (mol/g)
C _{A0}	initial concentration of A in bulk liquid phase (mol/cm ³)	C _{S2}	concentration of vacant sites of type S ₂ (mol/g)
C _{AS1}	adsorption concentration of A on active site S ₁	C _{T1}	total concentration of vacant sites of type S ₁ (mol/g)
C _B	concentration of B (mol/cm ³)	C _{T2}	total concentration of vacant sites of type S ₂ (mol/g)
C _{B0}	initial concentration of B in bulk liquid phase (mol/cm ³)	C _W	concentration of W, product species (mol/cm ³)
C _{BS1}	concentration of B on active sites of type S ₁ (mol/g)	C _{WS2}	concentration of W on active sites of type S ₂ (mol/g)
		E	product species E, benzylidene malononitrile

*For correspondence

K_A	adsorption equilibrium constant for A (cm^3/mol)
K_B	adsorption equilibrium constant for B (cm^3/mol)
K_E	adsorption equilibrium constant for E (cm^3/mol)
K_W	adsorption equilibrium constant for W (cm^3/mol)
M	mole ratio of C_{B0}/C_{A0}
$-r_A$	rate of reaction ($\text{mol cm}^{-3} \text{ min}^{-1}$)
W	product species W, water
w	catalyst loading (g/cm^3)
X_A	fractional conversion of A
t	time (min)

1. Introduction

Clean and green industrial processes can be developed by using solid catalysts which also lead to process intensification. Particularly in the manufacture of fine and speciality chemicals, homogeneous catalysts are still used which are polluting, and should be replaced by eco-friendly catalytic processes. In contrast with solid acids, solid bases are not so rampantly used in industrial practices despite their potential for production of bulk chemicals, fine and super-fine chemicals and pharmaceuticals and pharmacology, perfumeries and flavors.^{1–5} Homogeneous base catalyzed reactions constitute a large body organic transformations covering some named and common routes. Some of the well-known reactions have been studied using different solid bases; for instance, Knoevenagel^{6–8} and Claisen-Schmidt condensations,^{9,10} Michael addition,¹¹ trans-esterification,¹² aldol¹³ and retro-Aldol condensations,¹⁴ isomerizations,¹⁵ and alkylation.^{2,5} Efforts have been directed at developing new heterogeneous catalysts in many laboratories including our own to understand the nature of basicity, dual functionality and mechanisms through different sophisticated techniques.^{16,17} Particularly, hydrotalcites (HT) or layered double hydroxides (LDH) have been favored as solid bases to study a gamut of interesting reactions. For several reactions such as glycerol carbonate synthesis,^{8,18–22} and O-alkylations,^{23–25} supported base catalysts could be tailor-made to impart better activity and selectivity. Hydrotalcites have been modified as catalysts for making fine chemicals such as 4-O-aryloxy carbonates by alkali promoted alkaline earth metal oxides,²⁵ dehydrozingerone by hydrotalcite (HT),²⁶ guaifenesin using HT, calcined hydrotalcite (CHT), CHT/HMS, MgO, Al_2O_3 and K-ZrO_2 ,²⁷ vanillyl mandelic acid by silica encapsulated $\text{Mg}(\text{OH})_2$,²⁸ natural benzaldehyde by HT,²¹ 2-methoxy phenyl benzoate over alkali promoted HT,²⁹ veratraldehyde by La-Mg mixed oxide,³⁰ and dicamba ester over MgO .³¹ In Knoevenagel condensation, homogenous catalysts are having technical and environmental problems and

previously used solid catalyst like mesoporous zeolites, amino-functionalized silica, and silicon oxynitrides are useful only in polar solvents and may be deactivated by moisture and CO_2 .

As the foregoing suggests HTs and modified HTs have gained considerable attraction. It is observed that modification of hydrotalcite with zinc and titanium metal enhances ion exchange capacity and acido-basic properties of catalyst to impart better catalytic properties. There are numerous methods of synthesis of HTs including co-precipitation, sol-gel, template-assisted synthesis, decomposition of nitrates, etc. These methods inherently contain a number of steps to get the final form of catalyst which are laborious, and consume more quantity of reactants. Hence, different procedures have been suggested in the literature for making metal oxide or mixed oxides like HTs. Among them, combustion synthesis has become a powerful alternative for the synthesis of materials which not only render reproducible results but also involve less number of steps. Combustion synthesis gives fine nanoscale metal oxides depending on the source of fuel and ignition temperature. Combustion synthesis^{32,33} produces metal oxides with high surface area, pore volume and mesoporosity and therefore it is heralded as a vital method to synthesize different catalysts. Combustion synthesis requires fewer steps to prepare catalysts; pore radius and particle size can be kept under control according to the application for which it is to be used.

Base catalysts are very commonly used in aldol condensation; however, some base catalyzed reactions like Knoevenagel condensation of benzaldehyde and malononitrile could be studied using novel solid bases. Product of this reaction benzyldiene malononitrile has numerous applications in pharmaceuticals, pharmacology, biotech and perfumery industries. The current work includes synthesis of titanium and zinc modified hydrotalcite catalysts by using two different fuels in combustion synthesis, their characterization, effect of fuels on the activity of the catalyst, and application in Knoevenagel condensation of benzaldehyde and malononitrile to benzyldiene malononitrile. Reaction mechanism and kinetic model were also studied. In this work both synthesis of catalysts and their applications are new.

2. Experimental

2.1 Chemicals

Aluminum nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), magnesium nitrate hexahydrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), glycerol, zinc

Table 1. Preparation of different catalysts.

Catalyst	Catalyst-Fuel	Al(NO ₃) ₃ · 9H ₂ O mol	Mg(NO ₃) ₂ · 6H ₂ O mol	Titanium isopropoxide mol	Zinc nitrate mol	Fuel mol
Hydrotalcite-Glycerol	HT	0.016	0.048	-	-	0.051
TiMg ₄ Al ₂ O ₉ Glycine	Ti-HT-Glycine	0.016	0.032	0.008	-	0.054
ZnMg ₄ Al ₂ O ₈ Glycine	Zn-HT-Glycine	0.016	0.032	-	0.008	0.054
TiMg ₄ Al ₂ O ₉ Glycerol	Ti-HT-Glycerol	0.016	0.032	0.008	-	0.042
ZnMg ₄ Al ₂ O ₈ Glycerol	Zn-HT-Glycerol	0.016	0.032	-	0.008	0.042

Slurry thickening Temp. 80 °C, Combustion Temp. 500 °C, Calcination Temp. 650 °C.

nitrate, glycine, titanium tetraisopropoxide, nitric acid (70%), methanol, benzaldehyde and malononitrile were purchased from S.D. Fine Chemicals, Mumbai, India. All other analytical reagent grade chemicals were used without any further purification in the synthesis of catalysts.

2.2 Catalyst preparation

2.2a Hydrotalcite: The synthesis of hydrotalcite (Mg–Al–O mixed oxide) was achieved by dissolution of Al (NO₃)₃ · 9H₂O (0.016 mol) and Mg (NO₃)₂ · 6H₂O (0.048 mol) in glycerol/glycine (0.051 mol) as fuel using some water to make a paste. Al and Mg nitrate ratio was kept at 1:3. Surplus water was removed by heating the mixture at 80 °C in the crucible. It led to a thick paste which was then heated in a muffle furnace at 500 °C which resulted in spontaneous combustion. At 500 °C combustion takes place due to the fuel forming gaseous products which lead to the generation of a porous network of the solid material. Since glycine was used the combustion products were CO₂, H₂O and nitrogen. Oxides of the metals were formed.³⁴

The solid material after spontaneous combustion was then calcined at 650 °C for 3 h in a furnace.^{21,22} In combustion synthesis method metal nitrates act as oxidizers whereas carbonaceous fuels like glycine and glycerol as reducing agents. The fuel also acts as a complexant for metal cations increasing their solubility and preventing crystallization of dehydrated metal nitrate. These are sources of carbon and hydrogen for combustion. Different amounts of the fuel also affect morphology and acido-basic properties of catalyst because of the evolution of different quantities of gases. Sufficient amount of fuel is thus required for complete combustion as given by the stoichiometry below.^{34,35}

Reaction stoichiometry for best Ti-HT-Glycine:

Reaction stoichiometry for Ti-HT-Glycerol

Table 1 gives the preparation of Zn and Ti loaded catalysts *vis-à-vis* hydrotalcite. The composition of the materials is given there.

2.3 Reaction setup and procedure

Knoevenagel condensation reaction was carried out in a standard cylindrical glass reactor of 100 mL volume with 4-baffles and overhead stirrer. The stirrer was a 45° pitched blade turbine impeller connected to a speed regulator. The reactor was kept in a thermostatic oil bath to maintain the desired temperature. In a typical run, 0.0094 mol benzaldehyde (limiting reactant) and 0.028 mol malononitrile were introduced in the reactor to make total reaction volume of 20 mL with ethyl acetate as solvent. The reaction mixture was heated to 60 °C at 1000 rpm. The catalyst loading was 0.0025 g/cm³. The sample was filtered using a centrifuge and then it was diluted with ethyl acetate to make 20 mL sample and analyzed by GC (Chemito 1000) using BP-50 mid-polar column (25 mm x 30 m). Nitrogen was used as a carrier gas at a flow rate of 1.0 mL/min.

2.4 Catalyst characterization

All five catalysts were characterized by EDXS (JOEL JSM 6308LA Analytical scanning Microscope) using 10 kV voltage at a counting rate of 519 cps and energy range of 0–20 Kev and SEM images were procured. The textural analysis of catalysts was performed by nitrogen adsorption using a Micromeritics ASAP 2020 instrument. 10% v/v CO₂ in He and 10% v/v NH₃ in He TPD was used to determine basic and acidic site densities of catalysts, respectively. Bruker AXS diffractometer D8 advance Cu-Kα radiation (λ = 1.540562) was used to acquire powder XRD patterns of catalysts.

3. Results and Discussion

3.1 Catalyst characterization

3.1a SEM and EDXS: SEM images of all five catalysts are shown in Figure 1. The average particle size is in the range of 50–100 μm. These catalytic samples show

Figure 1. SEM images of different catalysts. (a) Zn-HT-Glycine, (b) Zn-HT-Glycerol, (c) Ti-HT-Glycine, (d) Ti-HT-Glycerol (all x2500), (e) HT-Glycerol (x500) (f) Reused Ti-HT-Glycerol.

Table 2. Composition of different catalysts using EDXS.

Element	Catalyst-Fuel									
	Ti-HT-Glycine		Ti-HT-Glycerol		Zn-HT-Glycine		Zn-HT-Glycerol		HT-Glycerol	
	Mass wt. %	Mol%	Mass wt. %	Mol %	Mass wt. %	Mol %	Mass wt. %	Mol %	Mass wt. %	Mol %
O	42.69	-	42.66	-	29.66	-	31.77	-	-	-
Mg	18.54	50.06	18.55	50.06	19.24	49.60	20.28	52.10	76.44	75
Al	20.76	25.26	20.79	25.26	6.97	8.09	10.37	12.00	23.56	25
Zn	-	-	-	-	44.14	42.31	37.37	35.90	-	-
Ti	18.1	24.68	18.0	24.68	-	-	-	-	-	-
Total	100	100	100	100	100	100	100	100	100	100

irregular morphology and non-agglomerated particles, but they are fairly uniform in size which is generally seen for materials synthesized by combustion method. Reused catalyst after the second cycle has retained its highly porous nature. EDXS was used to determine the complete composition of titanium, zinc, aluminum and magnesium. The ratio of composition of aluminum and magnesium was maintained constant as follows: (Al/Mg ratio of 1:3) in HT-Glycerol, (Al/Mg ratio of 1:2) in

Ti-HT with glycine and glycerol as fuels, (Al/Mg of 1:4) in Zn-HT with glycine and glycerol as fuels. The composition of different catalysts is given in Table 2.

3.1b Textural properties by nitrogen adsorption method: Nitrogen adsorption-desorption isotherm was found to be of type IV or V. This isotherm shows a small hill at high relative pressure, which is characteristic of mesoporous materials. Surface areas given

Table 3. Performance of different catalysts for Knoevenagel condensation of benzaldehyde and malononitrile with regard to textural properties, acidity and basicity.

Catalyst-fuel	Surface area (m ² /g)	Pore volume (cm ³ /g)	Acidity (mmol/g)	Basicity (mmol/g)	Conversion of benzaldehyde %	Selectivity %	Yield %
Ti-HT-Glycine	226.2	0.252	0.0145	1.244	66.9	97.6	65.0
Zn-HT-Glycine	132.4	0.339	0.0135	0.540	61.1	95.2	58.1
Zn-HT-Glycerol	148.6	0.446	0.0145	1.770	58.0	93.1	54.0
Ti-HT-Glycerol	45.6	0.227	0.719	1.085	57.0	92.0	52.4
HT-Glycerol	127.0	0.418	0.6603	1.371	58.0	91.5	53.0

Figure 2. Nitrogen BET adsorption-desorption profiles for different catalysts.

by nitrogen adsorption are 226.2, 132.4, 148.6, 45.6 and 127.0 m²/g for Ti-HT-Glycine, Zn-HT-Glycine, Zn-HT-Glycerol, Ti-HT-Glycerol, and HT-Glycerol, respectively (Table 3). Figure 2 also justifies that surface area for catalyst Ti-HT-Glycine is the largest among all. Pore size distribution shows that a major part of the surface area is contributed by pores ranging from 5 to 20 nm. It suggests the mesoporous character of catalysts. The complete explosive decomposition of the organic compound takes place in the case of glycine at a lower temperature as compared to glycerol. The stoichiometry also shows different quantities of gases are formed which lead to the different porous structure which is due to oxide formation. It enhances surface area and activity of the catalyst.

3.1c Acidity and basicity by TPD: In the CO₂ TPD, intermediate and strong basic sites are shown at some specific temperature by well-defined peaks (Figure 3) due to surface basic oxygen atoms for all catalysts used. Zn-HT-Glycine and Ti-HT-Glycine show moderate to strong basic sites from 200–400 °C. With NH₃-TPD some broad peaks are seen below 200 °C for all catalysts which indicate that some sites are of intermediate and weak acidic nature due to H⁺ ions linked with surface hydroxyl groups (Figure 4). Table 2 also includes both acidic and basic site concentrations for all catalysts which are related to the surface area. Ti-HT-Glycine catalyst shows even distribution of sites having the maximum surface area which are reflected in its activity. Results show that

Figure 3. CO₂-TPD thermograms for different catalysts.

Figure 4. NH₃-TPD thermograms for different catalysts.

due to the change in fuel from glycerol to glycine, acidity decreases and basicity increases which plays an important role in improving the activity of the catalyst.

3.1d Morphology properties by XRD: XRD is a beneficial technique to determine morphology, crystal size, purity and characteristics of any solid material. Figure 5 indicates the XRD pattern for Ti and Zn-HT with glycine and glycerol as fuels and HT-Glycerol with Al/Mg ratio of 1:2, 1:4 and 1:3, respectively. Incorporation of a tetravalent ion such as Zr⁴⁺ and Ti⁴⁺ in the structure, as a partial replacement of the M²⁺ or M³⁺ ions, was found to enhance the anion

exchange capacity as well as alter the acido-basic properties of the resulting mixed oxides.^{36,37} It has been reported that Zr⁴⁺ containing hydrotalcites such as Mg/Al, Zn/Al and also Ni/Al compounds have excellent catalytic properties and used in important reactions. In the case of Mg/Al, Al³⁺ is isomorphously substituted by Ti⁴⁺ in the brucite layer^{37–39} which has been also reported earlier. Calcination at 650 °C leads to the collapse of crystalline MgO type of structure reducing the intensity of peaks. Besides original LDH could reconstitute upon rehydration at atmospheric pressure and room temperature. Our XRD analysis (Figure 5) BET (Table 3) and SEM images (Figure 1) confirmed this behavior. In Figure 5 reflections at different 2θ

Figure 5. XRD patterns of Zn-HT, Ti-HT with Glycine and glycerol as fuels and HT-Glycerol.

Table 4. Analytical data by XRD for catalysts prepared by combustion method.

Catalyst	2 θ ^o	FWHM	Crystal size (nm)
Ti-HT-Glycine	43.88	1.804	4.98
Ti-HT-Glycerol	11.72	0.757	11.02
Zn-HT-Glycine	11.40	1.071	7.79
Zn-HT-Glycerol	34.28	1.32	6.58
HT-Glycerol	43.148	0.996	8.98

values indicate different metals in the catalysts (ICDD card number matching). Ti and Zn -HT with glycine and glycerol as fuels and HT-Glycerol reveal different reflections for different 2 θ values showing that catalysts have layered FCC, FCC, BCC, hexagonal, crystalline structure, respectively. Nanocrystalline nature of all catalysts can be seen by the broadness of peaks. The crystal size of the sample was estimated by using Scherrer's formula which is in the range of 4–11 nm for all catalysts (Table 4). The most active catalyst Ti-HT-Glycine possesses the smallest crystal size of 4.98 nm providing more active sites for reaction. Mg-Al-Ti LDH has been prepared by co-precipitation with di-, tri- and tetra-valent cations, such as different $\text{Al}^{3+}/\text{Ti}^{4+}$ ratio, and used as active visible-light photocatalysts.^{38,39} It is found that no hydrotalcite structure was formed for $\text{Ti}^{4+}/(\text{Ti}^{4+} + \text{Al}^{3+}) > 0.5$ and the substitution of Ti^{4+} for Al^{3+} in the layer increases the thermal stability of the resulting LDH materials.³⁶ In our case the Ti-HT-Glycine with $\text{Ti}^{4+}/(\text{Ti}^{4+} + \text{Al}^{3+}) = 0.494$ has retained HT structure with increased thermal stability.

3.2 Catalytic activity

Scheme 1 shows the reaction of benzaldehyde with malononitrile to produce benzylidene malononitrile.

3.2a Reaction scheme and effect of solvent: Synthesis of benzylidene malononitrile by Knoevenagel condensation of benzaldehyde and malononitrile was carried out by using various solvents such as ethyl acetate, methanol and toluene but the conversion of benzaldehyde was less after 4 h in all the solvents and also it was hampering the selectivity of benzylidene malononitrile. The effect of solvent is very complex, and there are a number of factors that influence the rate of reaction and selectivity of the product. This is because of the competitive adsorption of the solvent molecule on the catalyst surface. It can be determined by the δ value, which states that solvents with negative δ value have the very least interaction with a metal catalyst, whereas the interaction of an organic solvent increases with a change in δ value from negative to positive. Here, we can see that the value of δ increases in the following order: ethyl acetate < methanol < toluene. Ethyl acetate with a lower value of δ gives maximum conversion, whereas toluene gives the least conversion. Literature also shows that in the synthesis of benzylidene malononitrile by Knoevenagel condensation of benzaldehyde and malononitrile, ethyl acetate is commonly used as solvent due to its less interaction with catalyst, high recovery, low vapor pressure, high conversion and selectivity.⁴⁰

3.2b Efficacy of catalysts: The efficacy of the different modified catalysts was compared with HT-Glycerol.

Scheme 1. Overall reaction for the production of benzylidene malononitrile

Figure 6. Effect of different catalysts on conversion of benzaldehyde.

Figure 6 shows that the conversion of benzaldehyde is the highest (66.9%) with Ti-HT-Glycine due to more active sites on its surface. It is due to bigger surface area, active sites and high basicity of Ti-HT-Glycine. The characterization data supported this result. The blank test was also conducted without the use of catalyst which gave only 4% conversion of benzaldehyde in 7 h.

3.2c Effect of speed of agitation: The effect of speed of agitation was studied at 60 °C for a catalyst loading of 0.0025 g/cm³ (Figure. 7). It was found that in the range of stirrer speed 1000–1200 rpm, there was no effect on the rates of reaction. Both selectivity and conversion remained almost constant after 1000 rpm indicating the absence of mass transfer resistance. Selectivity to the product was 100%. Hence, all further experiments were carried out at 1000 rpm. A theoretical analysis of the assessment of external mass

transfer resistance, as given in some of our earlier work, confirmed that mass transfer resistance was negligible.

3.2d Effect of catalyst loading: The reaction rate is directly proportional to the loading of catalyst in the absence of external mass transfer resistance. The catalyst loading was changed from 0.0125–0.06 g corresponding to 6.25×10^{-4} – 3×10^{-3} g/cm³ on the basis of total reaction mixture volume (Figure 8). Benzaldehyde conversion increases as catalyst loading increases which owe to increase in the number of active sites in the same proportion. The selectivity was 100% in all cases. The initial rate of reaction increases with catalyst loading (Figure 9). However, from a catalyst loading range 0.05 to 0.06 g in the same total reaction mixture volume, there was no substantial increase in the final conversion and also selectivity of the product remained unaffected. It would mean the number of active sites available for reaction exceeds the number of moles of

Figure 7. Effect of speed of agitation on conversion of benzaldehyde.

Figure 8. Effect of catalyst loading on conversion of benzaldehyde.

Figure 9. Plot of initial rate versus catalyst loading showing linear relationship.

Figure 10. Effect of mole ratio of benzaldehyde to malononitrile on conversion of benzaldehyde.

Figure 11. Effect of temperature on conversion of benzaldehyde.

reactants beyond 0.05 g. All subsequent experiments were carried out using catalyst loading of 0.05 g which corresponded to 2.5×10^{-3} g/cm³ of the total volume of reaction.

3.2e Effect of mole ratio: During the reaction, the concentration of benzaldehyde and malononitrile was changed through the mole ratio of benzaldehyde and malononitrile in solvent ethyl acetate while keeping the liquid phase volume constant at 20 mL. Benzaldehyde was taken as the limiting reactant and the amount of malononitrile varied from 1:01 (benzaldehyde 0.0094 mol, malononitrile 0.01408 mol) to 1:03 (benzaldehyde 0.0094 mol, malononitrile 0.0422 mol). The overall reaction rate increased with increasing concentration of malononitrile (Figure 10). It indicates that the initial

rate of reaction is proportional to the concentration of malononitrile.

3.2f Effect of temperature: The effect of temperature was studied from 40 to 70 °C. The rate of reaction increased significantly with temperature and there was a substantial increase in the conversion which indicates that the reaction is controlled by the chemical kinetic step (Figure 11).

3.2g Reusability of catalyst: After completion of the reaction the catalyst was filtered off, refluxed with 10 mL ethyl acetate for 30 min, separated and again refluxed with 15 mL ethyl acetate to remove any adsorbed reactants and products from the pore space and surface of the catalyst. Thereafter it was dried at 120 °C, calcined at

Table 5. Reusability of Ti-HT-Glycine catalyst.

Run No.	Conversion of benzaldehyde (X_A) %	Selectivity of benzylidene malononitrile (S_C) %	Yield of benzylidene malononitrile (S_C) %
Fresh	66.8	96.4	64.4
First use	65.5	96.1	63.0
Second use	63.9	95.5	61.0

Table 6. Characterization of fresh and spent Ti-HT- Glycine catalyst.

Characterization Parameter	Fresh Ti-HT-Glycine	Spent Ti-HT-Glycine
Surface area (m ² /g)	226.2	210.6
Pore volume (cm ³ /g)	0.252	0.23
Pore diameter (nm)	9.12	9.10
Acidity (mmol/g)	0.015	0.014
Basicity (mmol/g)	1.24	1.22

650 °C for 3 h and cooled to room temperature. The catalyst was weighed to observe that there was a marginal loss which was made up by fresh catalyst for subsequent runs. The reusability study is given in Table 5. It is seen that catalyst activity and selectivity are maintained within experimental error. Comparative characterization of the fresh and spent catalyst after the second run is provided in Table 6. There was an insignificant difference for pore volume and pore diameter whereas, a slight decrease in the surface area, acidity and basicity was observed between fresh and spent catalyst. Thus the catalyst was found to be stable and reusable.

3.2h Reaction mechanism: Since the catalyst is bifunctional having weak acidic (S_1) sites and strong basic (S_2), a reaction mechanism was proposed as given in Scheme 2. In the proposed mechanism, the basic site (S_2) abstracts one proton from the active methylene group of malononitrile which is more acidic because of the presence of two strong electron-withdrawing nitrile (cyano) groups in the molecule. Thus, the conjugate base generated *in situ* is more stable as a result of conjugation with the two nitrile groups.⁴¹ This anion leads to a nucleophilic attack on to the carbonyl carbon atom of benzaldehyde attached on acidic site (S_1). The β -hydroxyl compound is generated when the negative charge over O picks up one proton from the catalyst and the catalyst is regenerated. The β -hydroxyl compound thus forms α,β -unsaturated dicyano compound on basic site (S_2) benzylidene malononitrile, through the elimination of one water molecule. It should be noted

that the C atom attached with the nitrile group designated as α carbon.

3.2i Kinetic model: Based on the above mechanism a kinetic model was developed for Knoevenagel condensation reaction in the absence of both external mass transfer and intraparticle diffusion resistances. Preliminary data were interpreted using many models and the following was observed to fit the data well. As explained earlier chemisorption of A (benzaldehyde) and B (malononitrile) takes place on two nearby vacant sites S_1 and S_2 , respectively, according to the Langmuir-Hinshelwood-Hougen-Watson (LHHW) mechanism to give E (benzylidene malononitrile, site S_2) and W (water, site S_1).

Adsorption of benzaldehyde A on vacant acidic site S_1 ,

Similarly, on another vacant basic site S_2 , malononitrile gets adsorbed as,

In 3rd step adsorbed species react to give products ES_2 and WS_1 on active sites as follows,

Finally, desorption of complexes formed ES_2 and WS_1 is represented by following reversible reactions

giving regeneration of active sites S_1 and S_2 finally.

The derivation of the rate equation is given in Supplementary Information (SI).

If the surface reaction controls the reaction, then the reaction rate of A is given by a second order rate equation:

$$-r_A = -\frac{dC_A}{dt} = k_{R_2} w C_A C_B \quad (6)$$

Scheme 2. Catalytic cycle for the Knoevenagel condensation over Ti-HT-Glycine (a – acid site, b – base site).

Figure 12. Validity of model: Kinetic plots for various temperatures.

Which on integration gives the following:

$$\ln \left[\frac{(M - X_A)}{M(1 - X_A)} \right] = k_{R_2} C_{A_0} w t = k t \quad (7)$$

Where X_A is fractional conversion of A and $M = \frac{C_{B_0}}{C_{A_0}}$, initial mole ratio of concentration of B to A

Figure 13. Arrhenius plot.

A plot of $\ln \left[\frac{(M - X_A)}{M(1 - X_A)} \right]$ versus time was made for different temperatures which are straight lines passing through origin which confirms that the reaction is second order and validates the kinetic model (Figure 12). The slopes of these lines k were used to make the Arrhenius plot (Figure 13). The apparent activation energy was found to be 10.01 kcal/mol which confirmed that

the reaction rate was controlled by intrinsic kinetics at the catalyst surface.

4. Conclusions

Al-Mg hydrotalcite (HT) was modified with Ti and Zn using glycine and glycerol as two different fuels in the combustion synthesis method. This is the first report which contains synthesis, full characterization and comparison of heterogeneous Ti-HT and Zn-HT with glycine and glycerol as fuels. All five catalysts including HT-Glycerol were evaluated in the Knoevenagel condensation between benzaldehyde and malononitrile to give benzylidene malononitrile as the product. Among these, Ti-HT-Glycine was the most active and selective in comparison with other reported catalysts. The study also shows that fuel plays an important role in determining the performance of the catalyst in the combustion method. It gave 67% conversion of benzaldehyde in 4 h at 60 °C with mole ratio 1:03 of benzaldehyde and malononitrile with a catalyst loading of 0.0025 g/cm³. LHHW model was fitted with weak adsorption of all species leading to second-order kinetics with apparent energy of activation 10.01 kcal/mol. The catalyst could be used thrice without loss of activity. Ti-HT-Glycine can be used for different base catalyzed industrial important heterogeneous reactions.

Supplementary Information (SI)

Supplementary information for this article is available at www.ias.ac.in/chemsci.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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