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# Structure-induced Lewis-base $Ga_4B_2O_9$ and its superior performance in Knoevenagel condensation reaction



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# ABSTRACT

Solid Lewis-base catalysis is important in the production of fine chemicals. A Lewis-base  $Ga_4B_2O_9$  was synthesized by high temperature solid state reactions. It exhibited a high yield (90 %) and a high stability in Knoevenagel condensation reactions, where several aldehydes were combined with malononitrile to form  $\alpha$ ,  $\beta$ unsaturated compounds through nucleophilic addition reactions. Reaction kinetics analyses indicated Knoevenagel condensation reactions over  $Ga_4B_2O_9$  catalyst obeyed a second-order characteristics and the calculated activation energy was ~61.6 kJ/mol, suggesting that Langmuir-Hinshelwood absorption pathway was probably employed. The structural evolution from  $Ga_4B_2O_9 \rightarrow GaBO_3 \rightarrow \beta$ -Ga<sub>2</sub>O<sub>3</sub> evidenced that the structureinduced basicity of  $Ga_4B_2O_9$  attributed to the special  $\mu_3$ -O atoms linked exclusively to 3 five-coordinated  $Ga^{3+}$ . This investigation proves a convincible structure-property correlation in Ga-based solid base materials and helps developing an alternative avenue towards the design of new intrinsic solid base catalysts.

# Introduction

Solid-base catalysts play a decisive role in green chemistry by providing an environmentally benign and sustainable route for the syntheses of fine chemicals and chemical intermediates [1-3]. In the late 1950s, the first solid base catalyst was reported in the isomerization of olefins with both an excellent conversion and selectivity, where alumina was treated with molten sodium in an inert atmosphere to provide Lewis basic sites [4]. Since then, solid-base-catalyzed organic reactions have been an interesting topic [5-18]. Typically, the traditional fivestep synthetic route of 4-methylthiazole was improved into two steps with an environmentally operation by applying a cesium-loaded zeolite catalyst [11]; a robust recyclable solid-base catalyst CsF·Al<sub>2</sub>O<sub>3</sub> catalyzes a 1,4-addition reaction from glycine derivatives to glutamic acid derivatives in mild conditions [12]. Although a great effort has been made, this field is less developed compared to solid acid catalysis. The functionality of solid bases and catalytic mechanism, especially in the precise preparation of solid materials with tunable electronic and physical structure, are always a challenge [19-23], thus the development of new types of solid bases is highly desired.

Recently, a potential Lewis base  $Ga_4B_2O_9$  was reported to have some interesting structure-induced basic sites. Different with some previously-reported solid-base catalysts,  $Ga_4B_2O_9$  is an intrinsic solid base, and its base-sites are reasonably proved to generate from a special

localized structure in the framework, which makes Ga<sub>4</sub>B<sub>2</sub>O<sub>9</sub> very stable and durable without some additional post-modifications. Ga<sub>4</sub>B<sub>2</sub>O<sub>9</sub> is a mullite-type borate, and its crystal structure and the related properties have been reported elsewhere [24-27]. As shown in Fig. 1, Ga<sub>4</sub>B<sub>2</sub>O<sub>9</sub> has four types of building blocks, such as GaO<sub>6</sub>, GaO<sub>5</sub>, BO<sub>4</sub>, BO<sub>3</sub>, among which, GaO<sub>6</sub> octahedra share edges to form one-dimensional chains along [010] direction. These edge-sharing chains along b axis are further cross-linked by three inter-chain groups, i.e. GaO<sub>5</sub>, BO<sub>3</sub> and BO<sub>4</sub> units, into a three-dimensional structure [24]. In fact, its structure within ac plane is disordered, but ordered along b axis. A preliminary study with DFT calculation suggests the  $\mu_3$ -O atoms linked with three 5coorindated  $Ga^{3+}$  act as the donor of electrons (see Fig. 1c) [25]. In general, the traditional solid bases include the defect-induced solids (alkaline metal treated oxides), Brönsted bases and metal-organic framework (MOF)-based solids. The major drawback is their low durability and thermal stability. Here Ga<sub>4</sub>B<sub>2</sub>O<sub>9</sub> was prepared with hightemperature solid state reactions, and its basic sites are structure-induced, intrinsically originating from the  $\mu_3$ -O atoms, thus is supposed to be a new type of Lewis base with an outstanding stability. In the current stage, the confirmation of the basicity from such  $\mu_3$ -O atoms is urgent.

Knoevenagel condensation reaction is a general route to the formation of C=C bond using active methylene compounds and aldehydes/ketones as reactants. It is also commonly used as a probe reaction or a determined proof to evaluate basic capacity in the base-

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**Fig. 1.** (a) Structure illustration of  $Ga_4B_2O_9$  with unsaturated coordination along *b*-axis; (b) octahedral chains along *a*-axis; (c)  $\mu_3$ -O atoms linked to five-coordinated  $Ga^{3+}$ .

catalyzed reactions, in which basic sites attract proton atoms from adsorbed methylene molecules to form carbanion intermediate [28]. Furthermore, Knoevenagel condensation reaction is a key step to produce several therapeutic drugs such as niphendipine and nitrendipine, as well as pharmacological products of calcium channel blockers and antihypertensives [29]. Traditionally, Knoevenagel condensation reaction was performed in a homogeneous liquid alkali system [30–32]. However, their applications are limited due to the environmental problems, including the post-treatment of waste liquid, equipment corrosion and product separation [33]. Given these restrictions, many heterogeneous catalysts have been attempted in Knoevenagel condensation reactions recently, including amine-functionalized molecular sieves [34,35], metal oxides [36,37], MOFs [38–41], N-doped carbon [42,43], and metal cation-exchanged zeolites [44].

As a successful alternative to homogeneous catalysis, heterogeneous catalysis has also been widely used in various type of catalytic organic reactions in recent years, such as Strecker reaction, acetylation reaction, N-formylation of amines and nitroarenes, alcohols dehydrogenation or dehydration, et al. [45–52]. Nevertheless, the complexity of heterogeneous catalyst system poses a new challenge to the understanding of the related reaction mechanism, and it is especially difficult for the insufficiently-investigated solid-bases system. Their feasibility and the structure-property relationship between catalytic sites and the involved active species still need a further explorations [53,54].

The main objective of this work is to understand the structure sensitivity of Lewis-base  $Ga_4B_2O_9$  in Knoevenagel condensation reaction and thus reveals the structure-property correlation in the Ga-based borates. A high yield (90 %) was achieved in a short time interval under the mild reaction conditions when using benzaldehyde and malononitrile as substrates, and the structural comparison along with the catalytic activity between  $Ga_4B_2O_9$ ,  $GaBO_3$  and  $\beta$ - $Ga_2O_3$  provided a solid proof to ascertain the actual active sites in  $Ga_4B_2O_9$ . Based on our observations and some previous reported results, a catalytic mechanism was proposed. More importantly, this work also hinted some gallium-based compounds with similar crystal structure may behave as the potential candidates in base-catalyzed reactions, which not only opens an avenue towards the development of new intrinsic solid base catalysts, but also a more in-depth understanding of reaction mechanism *via* a detailed insight on structure-property correlations.

# **Experimental section**

#### Catalyst preparation

 $Ga_4B_2O_9$  was prepared by high temperature solid state reactions, which was also described elsewhere [27]. In a typical run, 1 mmol of  $\beta$ - $Ga_2O_3$  (0.1874 g) was dissolved in 2 ml of concentrated HNO<sub>3</sub> in a closed system, then the obtained aqueous solution was dried into white

powder by gently heating in a hot plate. Afterward, 1.2360 g of boric acid powder was charged and the mixture was ground in an agate mortar. Finally, the resultant powder was placed in a corundum crucible and calcined in muffle furnace at 873 K for 10 h. After heating, the product was washed thoroughly with water to remove any soluble residuals. The pure Ga<sub>4</sub>B<sub>2</sub>O<sub>9</sub> sample was obtained after drying in an oven.

#### Catalyst characterization

Powder X-ray diffraction (XRD) data were collected with a PANalytical Empyrean powder diffractometer equipped with a PIXcel 1D detector (Cu Ka radiation 1.5406 Å). The cell parameters were refined by Le Bail fitting using TOPAS software package [55]. Scanning electron microscopy (SEM) was performed on a JSM-7800 F electron microscopy at an accelerating voltage of 2 kV and a working distance of 4.0 mm. Transmission electron microscopy (TEM) was employed on JEOL JEM-2100 F to observe the morphologies of as-prepared materials at an accelerating voltage of 200 kV. The Brunauer-Emmett-Teller (BET) method was employed to measure the surface area of Ga<sub>4</sub>B<sub>2</sub>O<sub>9</sub> with nitrogen adsorption-desorption at 77 K using a Quantachrome Quadrasorb SI analyzer. Temperature-programed desorption of carbon dioxide (CO2-TPD) was carried out in a Quantachrome ChemBET Pulsar instrument equipped with a thermal conductivity detector. Ga<sub>4</sub>B<sub>2</sub>O<sub>9</sub> catalyst (0.1 g) was pre-heated in He gas flow (90 mL·min<sup>-1</sup>) at 673 K for 1 h and then was exposed to CO<sub>2</sub> flow at the rate of 90 ml/min at 323 K for 1 h, following by He flushing for 1 h, finally CO<sub>2</sub> desorption data was executed in the temperature range of 323 – 923 K. The amount of CO<sub>2</sub> desorbed were determined using 0.01 M NaOH absorbent, following a titration with 0.005 M HCl standard solution in the presence of indicator.

#### Catalytic performance

Catalytic activity of the as-prepared  $Ga_4B_2O_9$  catalyst was evaluated using Knoevenagel condensation reaction. Benzaldehyde and malononitrile were selected as model substrates to afford benzalmalononitrite (**1a**), and the reaction equation was given in Scheme 1. Typically, 1 mmol of benzaldehyde and 1.2 mmol of malononitrile were dissolved into 4 ml anhydrous DMSO solvent in a 10 ml flask. After adding 30 mg of  $Ga_4B_2O_9$  catalyst into the reaction system, catalytic reaction was kept at 313 K in an oil bath under stirring. Meanwhile, inert protection gas N<sub>2</sub> was forced to pass through the flask during the reaction in order to prevent the oxidation of benzaldehyde. After a certain time interval of 30 min, reaction mixture was drawn out with a syringe equipped with an ultra-thin filter membrane to remove solid catalyst, the obtained liquid were analyzed with chromatography-mass spectrometry (GC–MS, Agilent 7890 N) to identify the molecular structure of the obtained product, and the mass spectrum was shown in



Fig. 2. (a) Le Bail fitting of powder XRD pattern. Blue circles, red and black lines represent the observed, calculated patterns, and the difference between them, respectively. The green bars below are the expected reflection positions; (b) SEM and (c) TEM images for the as-synthesized  $Ga_4B_2O_9$ .

Fig. S1 in the Supporting Information (SI). Similarly, the qualitative analyses of other 7 similar compounds were done and their corresponding mass spectra were also provided in Figs. S2-S8. The quantitative analysis of these involved reactants and products were performed on a gas chromatography (SHIMADZU GC2010 plus) equipped with an AOC20i auto-injector. A capillary column (HP-VOC, length 60 m; inner diameter 0.32 mm; film thickness 1.80 µm) was chosen to separate the mixed components at the following operation condition: 513 K for capillary column, 553 K for injector port, 563 K for FID detector. The total vield of product 1a is calculated by multiplying benzaldehyde conversion and product selectivity, while turnover number (TON) is calculated with the division of the moles of consumed substrate by the moles of used catalyst and reaction time. Nuclear magnetic resonance (NMR) spectra were employed to identify the molecular structure of some obtained products. <sup>1</sup>H NMR spectra were recorded on Agilent VNMRS (400 MHz) instrument using Deuterated dimethyl sulfoxide as the solvent and using tetramethylsilane (TMS) as an internal standard, and the obtained data were shown in Figs. S9-S16.

#### **Results and discussion**

#### Syntheses and structure of catalysts

The phase purity of as-synthesized Ga<sub>4</sub>B<sub>2</sub>O<sub>9</sub> sample was confirmed by powder XRD. As indicated in Fig. 2a, no impurity diffraction peak was observed for the as-synthesized Ga<sub>4</sub>B<sub>2</sub>O<sub>9</sub> sample, and all diffraction peaks can be indexed to a monoclinic lattice system with the space group *C*2/*m*. Le Bail fitting to the XRD pattern was performed to obtain the unit cell parameters (a = 15.406 Å, b = 5.765 Å, c = 11.016 Å,  $\beta = 135.24^\circ$ ), which are consistent with the previously-reported data [25,27]. The wide XRD diffraction peaks indicate that Ga<sub>4</sub>B<sub>2</sub>O<sub>9</sub> may crystallize in an extremely small particles. The SEM image in Fig. 2b and TEM image in Fig. 2c confirmed the above assumption, where the crystalline grains of Ga<sub>4</sub>B<sub>2</sub>O<sub>9</sub> are clustered-like and are comprised of some compact aggregates of nano-scaled needle, the length of the needle-shaped crystal is at micron level and the diameter is about tens of nanometers. Though this sample was prepared at a high temperature, Ga<sub>4</sub>B<sub>2</sub>O<sub>9</sub> has a large specific surface area. As shown in Fig. S17, the BET



**Fig. 3.** The yield of product **1a** and TON using benzaldehyde (BA) and malononitrile (MN) as reactants under different reaction conditions: (a) the influence of different solvents: 1 mmol benzaldehyde, 1.2 mmol malononitrile, 4 ml solvent, 30 mg  $Ga_4B_2O_9$  catalyst,  $N_2$ , 313 K, 30 min; (b) the influence of different temperature: 1 mmol benzaldehyde, 1.2 mmol malononitrile, 4 ml DMSO solvent, 30 mg  $Ga_4B_2O_9$  catalyst,  $N_2$ , 30 min; (c) the influence of different molar ratio (MN/BA): 4 ml DMSO solvent, 30 mg  $Ga_4B_2O_9$  catalyst,  $N_2$ , 30 min; (c) the influence of different molar ratio (MN/BA): 4 ml DMSO solvent, 30 mg  $Ga_4B_2O_9$  catalyst,  $N_2$ , 30 min; (c) the influence of different molar ratio (MN/BA): 4 ml DMSO solvent, 30 mg  $Ga_4B_2O_9$  catalyst,  $N_2$ , 313 K, 30 min; (d) the influence of different solid base catalyst: 1 mmol benzaldehyde, 1.2 mmol malononitrile, 4 ml DMSO solvent, 30 mg catalyst,  $N_2$ , 313 K, 30 min; (d) the influence of different solid base catalyst: 1 mmol benzaldehyde, 1.2 mmol malononitrile, 4 ml DMSO solvent, 30 mg catalyst,  $N_2$ , 313 K, 30 min; (d) the influence of different solid base catalyst: 1 mmol benzaldehyde, 1.2 mmol malononitrile, 4 ml DMSO solvent, 30 mg catalyst,  $N_2$ , 313 K, 30 min. The value right above the histogram is the measured basic-amount of these solid base catalysts.

surface area of Ga\_4B\_2O\_9 is estimated to be 40.7  $m^2/g$  according to  $N_2$  adsorption-desorption experiments. This high value of specific surface area is prominent in most bulk materials.

#### Catalytic performance

Catalytic properties of  $Ga_4B_2O_9$  were assessed using benzaldehyde and malononitrile as two substrates. The operation parameters, including solvent medium, temperature, molar ratio of reactants and catalyst type, were investigated in order to obtain an optimal reaction condition. First, five solvents with different polarity, including dimethyl sulfoxide (DMSO), N,N-dimethyl formamide (DMF), methyl alcohol (MeOH), ethyl alcohol (EtOH), propyl alcohol (PA) were chosen as the reaction medium because of their good compatibility with reactants. As shown in Fig. 3a, a minimum yield ( $\sim$  44 %) was obtained in DMF, while the highest one ( $\sim 90$  %) was achieved in DMSO. The reason of supreme yield in DMSO solvent may originate from the so-called "ion pair mechanism", that is, the high polarity of DMSO solvent is favorable to stabilize the formed carbon anion intermediates [56]. The influence of reaction temperature on Knoevenagel condensation reaction was also studied by ranging temperature from 293 to 333 K. As shown in Fig. 3b, reaction temperature has a positive effect on the reaction rates. The yield of product 1a and TON were significantly enhanced by increasing temperature from 293 to 313 K, indicating Knoevenagel condensation reaction was temperature-sensitive. Fig. 3c gives the influence of initial molar ratio of malononitrile and benzaldehyde changing from 0.6/ 1-1.4/1. The yield of 1a as well as TON rapidly increased by increasing the relative proportion of malononitrile, but it maintained the same level when their molar ratio exceeded 1.2/1. For the purpose of highlighting the predominant role of  $Ga_4B_2O_9$  catalyst, other five basic oxides with different basic amounts, such as  $CeO_2$ ,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, ZnO, SnO<sub>2</sub> and TiO<sub>2</sub>, were also evaluated with Knoevenagel condensation reaction under the similar reaction conditions. As shown in Fig. 3d,  $Ga_4B_2O_9$  has the moderate amount of basic sites, but exhibited the optimal catalytic activity. For example, the maximum TON over  $Ga_4B_2O_9$  is nearly 32 times higher than using TiO<sub>2</sub>.

In order to examine the universality of  $Ga_4B_2O_9$  in Knoevenagel condensation reaction, another 7 different aromatic aldehyde substrates were employed under the same reaction conditions, and the obtained results are summarized in Table1. In most cases,  $Ga_4B_2O_9$  catalyst exhibited the superior yield and product selectivity (> 99 %). When these aromatic aldehydes with an electron donor group were used, such as methyl or methoxy, (entry 7–8 in Table 1), catalytic activity decreased accordingly, which attributes to their stronger capacity of giving electrons and thus suppresses the combination between the substituted benzaldehydes and carbanions intermediate [20]. On the contrary, if the aldehydes with electron-withdrawing groups were selected as substrates, such as  $-NO_2$ , -Br, -OH groups, the product yield will remain at a high level.

#### Catalytic recyclability and reaction kinetics

Catalyst recyclability is one of the most important aspects to determine catalyst stability and life time. In this regard, the reusability

#### Table 1

Knoevenagel condensation reaction between some aldehydes and malononitrile in the presence of  $Ga_{4}B_{2}O_{9}$  catalyst.



Reaction conditions: 1 mmol aldehyde, 1.2 mmol malononitrile, 4 ml DMSO solvent, 30 mg Ga<sub>4</sub>B<sub>2</sub>O<sub>9</sub> catalyst, N<sub>2</sub>, 313 K, 30 min.

and stability of  $Ga_4B_2O_9$  catalyst was examined by the repetitive usage under the same reaction conditions. After each cycle, the solid catalyst was separated by centrifugation followed by water-washing. The recovered catalyst was dried and activated at 373 K for 60 min prior to the next run. As shown in Fig. 4a, there is no obvious decrease in the yield of product **1a** after 10 cycles. The powder XRD pattern of the recovered  $Ga_4B_2O_9$  (Fig. 4b) remained almost the same with the fresh catalyst, confirming an excellent structure stability of  $Ga_4B_2O_9$  in Knoevenagel condensation reaction.

The kinetic parameters of Knoevenagel condensation reaction were calculated from the linear fitting on the experimental data obtained under different temperatures, and the fitted curves were plotted in Fig. 5. The time-dependent curve of product yield in Fig. 5a gave a typical characteristics of the second-order reaction. After a nonlinear fitting, an empirical rate equation can be established as following:

$$k_2 t = \frac{1}{a-b} \ln \frac{b(a-x)}{a(b-x)} \tag{1}$$

where *x* is the concentration of product **1a**, *t* is reaction time,  $k_2$  is reaction rate constant, a and b represent initial concentration of malononitrile and benzaldehyde, respectively. It can be drawn from the plots that there has a good linear relation between reaction time *t* and concentration expression of  $\ln[(a-x)/(b-x)]$ , indicating Knoevenagel condensation reaction over Ga<sub>4</sub>B<sub>2</sub>O<sub>9</sub> obeys the second-order reaction kinetics [57]. Fig. 5b shows some kind of function relation of temperature *T* and the corresponding reaction rate constant *k*, and there has a quasi-linear plot between  $\ln(k)$  and  $T^{-1}$ . According to Arrhenius empirical formula [In  $k = \ln A - E_a/(RT)$ ], the apparent activation energy  $E_a$  can be deduced from the slope of the fitting curve after a linear regression, the final calculated  $E_a$  is ~61.6 kJ/mol. The lower apparent activation energy  $E_a$  suggests Ga<sub>4</sub>B<sub>2</sub>O<sub>9</sub> can efficiently activate the involved substrate molecules and thus haste the reaction rates in Knoevenagel condensation reaction.

#### Active sites and reaction mechanism

In order to identify the actual active sites in the framework of  $Ga_4B_2O_9$ , a successive thermal treatment was performed under the ambient pressure to demonstrate the evolution process of the involved crystal phase. Fig. 6a gives the powder XRD patterns of thermally-treated  $Ga_4B_2O_9$  sample from 873 K to 1033 K.  $Ga_4B_2O_9$  has a high thermal stability and remained its original structure until temperature reached 993 K. Beyond this critical temperature,  $Ga_4B_2O_9$  will firstly decompose into GaBO<sub>3</sub>, which occurs within a very narrow temperature range from 1013 to 1033 K, then it further decomposed into  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> above 1033 K. Fig. 6b gives the corresponding catalytic yields over  $Ga_4B_2O_9$ ,  $GaBO_3$  and  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> catalysts. Surprisingly, the results indicated catalytic activity have a tremendous change for these three Gacontaining catalysts. The yield was 90 %, 17 %, 17 % for  $Ga_4B_2O_9$ ,



Fig. 4. (a) Catalytic behavior of Ga<sub>4</sub>B<sub>2</sub>O<sub>9</sub> for 10 consecutive cycles; (b) powder XRD for fresh and recovered catalyst, respectively. Reaction conditions: 1 mmol benzaldehyde, 1.2 mmol malononitrile, 4 ml DMSO solvent, 30 mg Ga<sub>4</sub>B<sub>2</sub>O<sub>9</sub> catalyst, N<sub>2</sub>, 313 K, 30 min.



**Fig. 5.** (a) Time-dependent of product concentration in Knoevenagel condensation catalyzed over  $Ga_4B_2O_9$  at 313 K and the obtained empirical equation from the linear fitting; (b) the apparent activation energy  $E_a$  calculated from Arrhenius formula though the linear regression of ln *k* and  $T^{-1}$ . Reaction conditions: 1 mmol benzaldehyde, 1.2 mmol malononitrile, 4 ml DMSO solvent, 30 mg  $Ga_4B_2O_9$  catalyst, N<sub>2</sub>, 313 K.



Fig. 6. (a) X-ray diffraction patterns of powdered  $Ga_4B_2O_9$  treated at different temperatures and (b) the corresponding yield of the target product in Knoevenagel condensation reactions. Reaction conditions: 1 mmol benzaldehyde, 1.2 mmol malononitrile, 4 ml DMSO solvent, 30 mg  $Ga_4B_2O_9$  catalyst,  $N_2$ , 313 K, 30 min.

GaBO<sub>3</sub> and  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>, respectively. In fact, if the crystal structure and the coordination microenvironment of these three catalysts have been considered, these vastly different catalytic results can also be well elucidated.

As described above, the structure of Ga<sub>4</sub>B<sub>2</sub>O<sub>9</sub> features with 5-fold coordinated Ga<sup>3+</sup> (GaO<sub>5</sub>) and 6-fold coordinate Ga<sup>3+</sup> (GaO<sub>6</sub>). The  $\mu_3$ -O atoms linked exclusively to three 5-coordinated Ga<sup>3+</sup> are intrinsic and seem to function as the potential basic sites. For other two Ga-containing compounds, GaBO<sub>3</sub> and  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> have no similar GaO<sub>5</sub> coordination units. GaBO<sub>3</sub> crystallizes in a trigonal crystal system with lattice constants *a* = 4.568 Å, *c* = 14.182 Å and *V* = 256.3 Å<sup>3</sup> in space group *R*-3*c* [58]. As shown in Fig. 7a, GaBO<sub>3</sub> has only one type of Ga-based building unit (GaO<sub>6</sub>), and these GaO<sub>6</sub> octahedra-chains are interlinked by sharing the vertex of triangular BO<sub>3</sub> to form a three-dimension structure.  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> can be indexed with a monoclinic lattice (space group *C2/m*) and the cell lattice parameters are *a* = 12.214 Å, *b* = 3.037 Å, *c* = 5.798 Å,  $\beta$  = 103.83° and *V* = 208.85 Å<sup>3</sup> [59]. Fig. 7b

indicates that the framework of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> is constructed by two type of building units, i.e. 4-coordidated GaO<sub>4</sub> units and 6-coordidated GaO<sub>6</sub> units, these two type of building units are further interconnected into a three-dimensional structure through the vertex-sharing oxygen atoms. DFT calculations for Ga<sub>4</sub>B<sub>2</sub>O<sub>9</sub> revealed the oxygen atoms adjacent to three GaO<sub>5</sub> groups have a strong electronegativity and incline to act as the donors of electron pair, thus being active basic sites in the framework of Ga<sub>4</sub>B<sub>2</sub>O<sub>9</sub> [25]. After a high-temperature calcination, all GaO<sub>5</sub> units in Ga<sub>4</sub>B<sub>2</sub>O<sub>9</sub> were re-arranged into GaO<sub>6</sub> and/or GaO<sub>4</sub> units, such a coordination style transformation has resulted into the complete loss of basic centers in the GaBO<sub>3</sub> and  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>. The structural evolution of these three compounds also provide a powerful evidence to ascertain the actual catalytic sites in Ga<sub>4</sub>B<sub>2</sub>O<sub>9</sub> for Knoevenagel condensation reaction.

Temperature-programmed desorption (TPD) using  $CO_2$  as probe molecules was employed to characterize surface basicity in the purpose of further elucidating the origin of the structure-induced Lewis basicity



Fig. 7. Schematic illustration for the structure of (a) GaBO<sub>3</sub> and (b)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> along the *b*-axis, purple octahedron is GaO<sub>6</sub>, yellow tetrahedron is GaO<sub>4</sub>.



Fig. 8. (a)  $CO_2$ -TPD profiles of as-synthesized  $Ga_4B_2O_9$ ,  $GaBO_3$  and  $\beta$ - $Ga_2O_3$ ; (b) the linear dependence on product yield and the added amount of hydrogen chloride. Reaction conditions: 1 mmol benzaldehyde, 1.2 mmol malononitrile, 4 ml DMSO solvent, 30 mg  $Ga_4B_2O_9$  catalyst,  $N_2$ , 313 K, 30 min.

in the above-mentioned three catalysts. As shown in Fig. 8a, compared to GaBO<sub>3</sub> and  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>, Ga<sub>4</sub>B<sub>2</sub>O<sub>9</sub> possesses an obvious characteristic desorption peak at 721 K, indicating the presence of numerous basic sites. After a phase-transition from  $Ga_4B_2O_9$  into  $GaBO_3$  and  $\beta$ - $Ga_2O_3$ , nearly all the surface basic sites disappeared, indicating the superior base-catalyzed property in Ga<sub>4</sub>B<sub>2</sub>O<sub>9</sub> largely comes from the special connection mode of GaO<sub>5</sub> units. On the contrary, if these basic active sites are selectively occupied by a small amount of acidic poison, catalytic activity will presumably have a deep drop [13,60]. According to this assumption, hydrochloric acid, as an acidic impurity reagent, was added to reaction system. As shown in Fig. 8b, a linear decreasing on the product yield can be observed along with continuously adding hydrochloric acid. When exceeding a critical point, the product yield was kept to nearly zero. In conclusion, catalytic activity in Knoevenagel condensation reaction largely depends upon catalyst basicity. As the actual catalytic centers, GaO<sub>5</sub> coordination mode functions as a highly

effective activation sites in base-catalyzed reactions and therefore provides an alternative and potential candidate.

The above results evidenced the instinct basic-site structure localized in the framework of  $Ga_4B_2O_9$  catalyst, these basic sites can be accessible by the reactant molecules and are responsible to activate malononitrile. Based on our results and some previous literatures [19,57,60], a base-catalyzed mechanism has been presented in Fig. 9. Because the  $O^{2-}$  atom in the distorted  $GaO_5$  polyhedron exhibits a relatively lower Bader charge, which conclude Lewis base sites are located at the oxygen atoms linked with 5-coordinated  $Ga^{3+}$ , malononitrile, as an electrophilic molecule, is favorably adsorbed and activated in the sites of  $\mu_3$ -O atom, then a proton is abstracted from this activated methylene molecule and promote the formation of the corresponding carbanions. Because the 5-fold  $Ga^{3+}$  of  $Ga_4B_2O_9$  can partially polarize the C=O bond in benzaldehyde molecule, therefore, this formed carbanion subsequently will approach an activated



Fig. 9. Proposed mechanism for Knoevenagel condensation reaction.

benzaldehyde molecule, which is absorbed in the neighboring Ga site in the GaO<sub>5</sub> group, to undergo a nucleophilic attack and form a new C–C bond. After a subsequent molecular rearrangement, the cleavage of water from the formed benzylidene malononitrile intermediate will lead to the formation of  $\alpha,\beta$ -unsaturated compound with C=C bond [26,40,61].

#### Conclusion

In summary, a mullite-type Ga<sub>4</sub>B<sub>2</sub>O<sub>9</sub> catalyst, as an intrinsic Lewis solid base, has been prepared through high temperature calcination method. The special connection mode in  $Ga_4B_2O_9$ , i.e.  $\mu_3$ -O atoms bonding with 3 neighboring Ga atoms in GaO<sub>5</sub> groups, has endowed this material with a large amount of basic sites in the framework, thus an excellent catalytic performance (90 % yield) was achieved in Knoevenagel condensation reaction under the mild reaction conditions. Compared to other conventionally-used solid-base catalysts, Ga<sub>4</sub>B<sub>2</sub>O<sub>9</sub> exhibited a superior catalytic efficiency. The kinetic analysis indicated that Knoevenagel condensation reaction is characteristic of secondorder reaction, and also has a lower apparent activation energy in the presence of Ga<sub>4</sub>B<sub>2</sub>O<sub>9</sub>. From the structural evolution from  $Ga_4B_2O_9 \rightarrow GaBO_3 \rightarrow \beta - Ga_2O_3$ , as well as the experiment of active basic sites poisoning by acid additive species, the actual active sites were further ascertained and evidenced. Based on above observations, the relationship between the local structure of  $Ga_4B_2O_9$  and its catalytic activity has been well established, and a plausible mechanism was proposed. Despite of still some limitations in the observation of active intermediates through in-situ method, this investigation will bring a deep understanding on some special structure-induced property and thus helps to design and fabricate some similar-type solid base catalysts, a future effort is still needed to enhance the basicity of  $O^{2-}$  in some bulk-type solid Lewis bases, either through morphology controllable synthesis or transition metal-doping, thus extends the wide application in the industrial field of acid-base catalysis chemistry.

## CRediT authorship contribution statement

Yao Yang: Writing - original draft, Investigation. Duo Wang: Investigation. Pengfei Jiang: Formal analysis. Wenliang Gao: Writing - review & editing, Supervision. **Rihong Cong:** Supervision. **Tao Yang:** Writing - review & editing, Supervision, Project administration.

## **Declaration of Competing Interest**

There are no conflicts to declare.

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#### Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2020.110914.

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