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Dehydrogenation of propane over hydrothermal synthesized Ga₂O₃– Al₂O₃ catalyst in the presence of carbon dioxide

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Hydrothermal synthesis method was adopted to prepare a highly active Ga_2O_3 - Al_2O_3 catalyst (GA-HS), which displayed superior catalytic performance for dehydrogenation of propane to propylene in the presence of CO_2 (DHP- CO_2). The highest propane conversion on GA-HS was 35.2%, which was much 10 higher than the catalysts prepared using grind-mixture method (8.7%) or coprecipitation method (26.2%).

Moreover, propylene selectivity over GA-HS catalyst was higher than that over other catalysts in a period of 9 h reaction. These catalysts were characterized by N₂ physical adsorption, ICP-AES, XRD, TGA, TEM, SEM, DRIFT, Py-FTIR, NH₃-TPD, XPS, ²⁷Al MAS NMR and ⁷¹Ga MAS NMR techniques. The characterization data indicated that hydrothermal treatment increased the surface area, expanded the pore ¹⁵ size and promoted the formation of more tetrahedral Ga ions and generation of more medium-strong Lewis acid sites. Furthermore, this catalyst mainly displayed amorphous sponge-like morphology as well as a new morphology that some pieces were covered with amorphous nanoparticles. The superior activity of GA-HS was attributed to higher surface area of this catalyst and larger amount of tetrahedral Ga ions (Ga³⁺ and probably Ga^{$\delta+$} δ < 2) related to medium-strong Lewis acid sites.

20 1. Introduction

At present, urgent demand of propylene has drawn academic and industrial sectors' attention to deeply investigating the catalytic dehydrogenation of propane to propylene, for it represents a way in which more expensive alkenes can be produced economically

- ²⁵ from low-cost saturated hydrocarbons.^{1, 2} However, the dehydrogenation of propane has inherent disadvantages such as thermodynamic limitations for propane conversion, high energy requirements ascribed to endothermic reaction and limited catalytic stability in virtue of coke formation, etc.^{3, 4} Recently,
- ³⁰ oxidative dehydrogenation of propane with oxygen as an alternative process for propylene production offers a new promising technology in term of its energy-saving. By using oxygen as oxidant, the dehydrogenation can be proceeded well, but dramatic decrease of propylene selectivity due to excessive
- ³⁵ propane oxidation is still a problem.² Considering that, CO₂ as a mild oxidant is used to develop a safer and more economical process for propane dehydrogenation.⁵⁻⁷ With introduction of CO₂, the dehydrogenation efficiency is increased because of the new additional production process of propylene: a direct surface
- ⁴⁰ redox mechanism in which the catalyst undergoes reduction (by propane) and reoxidation (by carbon dioxide) cycles⁸⁻¹⁰ or a more complex reaction pathway involving a simple dehydrogenation followed by the reverse water gas shift (RWGS) reaction.¹¹⁻¹³
- Ga₂O₃-containg catalysts have been considered for alkane ⁴⁵ oxidative dehydrogenation processes due to their relatively good catalytic performance.¹⁴⁻³⁴ This was verified by Nakagawa *et al.*³⁵ According to their result, the commercial Ga₂O₃ showed higher

activity in the dehydrogenation of ethane to ethylene in the presence of CO₂, compared with Cr₂O₃ and V₂O₅ catalysts. ⁵⁰ Zheng *et al.*³⁶ investigated dehydrogenation of propane to propylene in the presence of CO₂ (DHP-CO₂) over four polymorphs of gallium oxides. They thought that the superior performance of β-Ga₂O₃ catalyst was ascribed to an abundance of surface medium-strong Lewis acid sites related to the unsaturated 55 Ga³⁺ cations and the conjugated effect of proton and oxide. The optimal propane conversion and propylene selectivity could achieve to 23% and 95% respectively, at 500 °C with feed gas mixture (CO₂/C₃H₈ molar ratio = 2:1) and flow rate of 3 L g⁻¹ h⁻¹. Based on that, supported gallium oxide catalysts (Ga₂O₃/TiO₂, 60 Ga₂O₃/Al₂O₃, Ga₂O₃/SiO₂, Ga₂O₃/ZrO₂ and Ga₂O₃/MgO) were also used for dehydrogenation of propane to propylene with CO₂ by Bingjun Xu et al.³⁷ It was found that Ga₂O₃/TiO₂, Ga₂O₃/Al₂O₃, and Ga₂O₃/ZrO₂ showed a stronger ability for the dehydrogenation of propane than Ga2O3/SiO2 and Ga2O3/MgO, 65 due to the abundant medium-strong Lewis acid sites on these catalysts' surface and special interactions between the support and Ga₂O₃. Ga₂O₃/TiO₂ showed the highest activity, and the propane conversion over this catalyst highly achieved to 39% at 600 °C with feed gas mixture (CO₂/C₃H₈ molar ratio= 2:1) and ⁷⁰ flow rate of 6 L g⁻¹ h⁻¹. Michorczyk *et al.*³⁰ prepared ordered mesoporous Ga2O3 and Ga2O3-Al2O3 by nanocasting, which were used as effective catalysts for DHP-CO2. The results revealed that the pure mesoporous gallium and gallium-aluminum oxides (Ga/Al = 4:1) exhibited a promising catalytic performance in the 75 DHP-CO₂. Over the most active materials, propylene was

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produced with the yield of 10-18% and high selectivity of 91-95% during 4 h on stream at 550 °C with feed gas mixture (CO₂/C₃H₈ molar ratio= 5:1) and flow rate of 9 L $g^{-1}h^{-1}$. Moreover, Chen et al.11, 12 studied the effect of preparation method and treatment 5 process on the activity and stability of Ga₂O₃-containg catalysts for the dehydrogenation of propane. The results suggested that larger amount of surface Ga³⁺ sites with weak Lewis acidity were presented on gallia-alumina solid solution prepared using coprecipitation method than that on the Ga₂O₃-Al₂O₃ oxide 10 catalysts prepared using physical mixture method, thereby leading to its better performance in propane dehydrogenation with CO₂. It was found that the initial conversion of propane and selectivity of propylene over Ga₈Al₂O₁₅ were 49.7% and 91.7% respectively, at 500 °C with feed gas mixture (CO₂/C₃H₈ molar 15 ratio = 2:1) and flow rate of 3 L $g^{-1} h^{-1}$. For the sake of deeply understanding this reaction, many researchers³⁶⁻³⁸ drew their attention to investigating the influence of surface Ga³⁺ in Ga₂O₃containg catalysts on dehydrogenation of propane. And their results suggested that hydrocarbon activation proceeded on low-20 coordinated Ga³⁺ cations, accordingly forming propyl-Ga species,36, 37 and the dehydrogenation products were then generated via subsequent decomposition of the resulting propyl-Ga species. Specifically speaking, the low-coordinated Ga³⁺ sites over gallium oxide were highly effective in the heterolytic 25 dissociative adsorption of propane, because of the very strong polarizability of the C-H bonds resulted from perturbation of propane on the low-coordinated Ga³⁺ sites.³⁹ It's obvious that more active catalysts for propane dehydrogenation can be obtained by getting a higher population of low-coordinated ³⁰ surface Ga^{3+} sites in the Ga_2O_3 -containg catalysts.

In this work, a facile hydrothermal synthesis method was adopted to prepare a Ga₂O₃-Al₂O₃ catalyst for DHP-CO₂. The asprepared catalyst displayed better catalytic performance than the catalysts prepared using grind-mixture method or coprecipitation ³⁵ method. We have in-detail rationalized the results by various characterizations such as N₂ physical adsorption, ICP-AES, XRD, TEM, TGA, SEM, DRIFT, Py-FTIR, NH₃-TPD, XPS, ²⁷Al MAS NMR and ⁷¹Ga MAS NMR techniques, and aimed to unveil the correlations between the structure and physical properties of ⁴⁰ Ga₂O₃-Al₂O₃ catalyst and its activity for propane dehydrogenation

2. Experimental section

2.1 Catalyst preparation

Herein, Ga_2O_3 - Al_2O_3 catalysts as well as the simple oxide of $45 Ga_2O_3$ and Al_2O_3 were prepared using different methods as follows.

Ga₂O₃ and Al₂O₃ can be obtained from Ga(NO₃)₃ and Al(NO₃)₃ respectively through the same treatment of drying at 120 °C for 8 h in constant temperature oven and subsequent ⁵⁰ calcinations at 550 °C for 5 h (from room temperature to 550 °C at a ramp rate of 3 °C/min) under static air in a muffle oven.

Grind-mixture method: 0.01 mol Ga(NO₃)₃ and 0.02 mol Al(NO₃)₃ (Ga/Al = 1:2) as the precursors were firstly mixed and ground, followed by drying at 120 °C for 8 h in constant ⁵⁵ temperature oven. The resulting mixture was heated to 550 °C

from room temperature at a ramp rate of 3 °C/min, and kept for 5

h under static air in a muffle oven, the catalyst was obtained and defined as GA-GM.

Coprecipitation method: the Ga_2O_3 - Al_2O_3 catalyst was ⁶⁰ prepared through an alcoholic coprecipitation pathway.⁴⁰ In a typical synthesis, 0.01 mol $Ga(NO_3)_3$ and 0.02 mol $Al(NO_3)_3$ (Ga/Al = 1:2) were completely dissolved in 40 mL ethanol. Then, 40 mL concentrated aqueous ammonia (28 wt%) was added dropwise to above ethanol solution. The resulting suspension was ⁶⁵ filtrated and washed by ethanol. After that, the cake was dried at 120 °C for 8 h in constant temperature oven, followed by calcination at 550 °C for 5 h (from room temperature to 550 °C at a ramp rate of 3 °C/min). The obtained catalyst was defined as GA-CP.

⁷⁰ Hydrothermal synthesis method: 0.01 mol Ga(NO₃)₃ and 0.02 mol Al(NO₃)₃ (Ga/Al = 1:2) were completely dissolved in 40 mL ethanol. Then, 40 mL concentrated aqueous ammonia (28 wt%) was added dropwise to above ethanol solution. The resulting suspension was transferred into 200 ml Teflon cup inserted in ⁷⁵ stainless steel autoclave, then heated to 170 °C from room temperature at a ramp rate of 10 °C/min and kept for 24 h. After that, the crystalline product was washed repetitively with ethanol, followed by drying at 120 °C for 8 h in constant temperature oven, and calcined at 550 °C for 5 h under static air like that of ⁸⁰ coprecipitation method. The obtained catalyst was defined as GA-HS.

Compared with GA-HS, pure Ga (G-HS) and Al (A-HS) were prepared using hydrothermal synthesis method. Moreover, Ga₂O₃-Al₂O₃ materials with different Ga/Al molar ratios (1:1 and ⁸⁵ 2:1) were also prepared by grind-mixture method, coprecipitation method and hydrothermal synthesis method, defined as G1A1-GM, G2A1-GM, G1A1-CP, G2A1-CP, G1A1-HS and G2A1-HS respectively.

2.2 Catalyst characterization

⁹⁰ The textural properties of catalyst were measured by N₂ physical sorption at 77K using a Tristar 3000 machine. Surface areas were calculated by the BET method and micro-, meso-, and macropore volumes were calculated by the t-plot method.

The powder X-ray diffraction (XRD) patterns were measured ⁹⁵ on a Rigaku MiniFlex II X-ray diffractometer using CuK α radiation. The anode was operated at 40 kV and 40 mA. The 2 θ angles were scanned from 10° to 70°.

Diffuse reflectance infrared spectra (DRIFT) measurements were performed using a Bruker Tensor 27 instrument with a MCT ¹⁰⁰ detector (64 scans, 4 cm⁻¹). Simply, 20 mg of catalyst was put it in an infrared cell with KBr windows for *in-situ* treatments. The DRIFT spectra were recorded after treating the catalyst at 300 °C for 1 h with a flow of argon.

Pyridine-adsorbed Fourier Transform Infrared Spectroscopy ¹⁰⁵ (Py-FTIR) was used to determine the amount of Brønsted acid sites and Lewis acid sites using Bruker Tensor 27 equipment. 20 mg of catalyst was pressed into a regular wafer (R = 1.3 cm) and then put in an infrared cell. The infrared spectrum was recorded after sample treatment at 400 °C for 2 h under vacuum, wherein ¹¹⁰ this spectrum was used as background for the adsorbed pyridine experiments. Pyridine was then adsorbed to a 5.0×10^{-2} Pa equilibrium pressure at 40 °C. FTIR spectra were recorded after consecutive evacuation at 400 °C.

The temperature-programmed desorption of ammonia (NH₃-

TPD) was used to test the amount and strength of the Lewis acid or Brønsted acid sites of as-prepared catalysts in TP-5080 chemisorption instrument. The catalyst (100 mg) was pre-treated at 500 °C under a flow of N₂ (30 ml/min) for 2 h and then cooled s down to 100 °C. Then NH₃ was introduced into the flow system.

The TPD spectra were recorded after about 1h evacuation time until the baseline of TCD signal is steady at a ramp rate of 10 °C/min from 100 °C to 600 °C.

X-ray photoelectron spectroscopy (XPS) was used to analyse to the change of surface composition measured by AXIS ULTRA DLD equipment. The binding energy values were corrected for charging effect by referring to the adventitious C1s line at 284.5 eV.

The chemical compositions (Al and Ga) of as-prepared samples 15 were determined by an inductively coupled plasma-atomic emission spectrometer (ICP-AES) method using Thermo iCAP 6300 equipment.

⁷¹Ga MAS NMR measurements were performed on Bruker AVANCE III 600 MHz equipment. ⁷¹Ga MAS NMR spectra ²⁰ were obtained by a single pulse length of $\Pi/6$, and Ga chemical shifts were referenced to Ga(NO₃)₃.

²⁷Al MAS NMR measurements were performed on Bruker AVANCE III 600 MHz equipment. ²⁷Al MAS NMR spectra were obtained by a single pulse length of Π/6, and Al chemical shifts ²⁵ were referenced to Al(NO₃)₃.

Transmission electron microscopies (TEM) were performed using a JEM-2100 transmission electron microscope.

Scanning electron microscopy (SEM) images were obtained for morphologic identification using a JSM-7001F.

³⁰ Pulsed reaction technique was used to measure the activities of these catalysts and carried out on chemisorption instrument (TP-5080) and OMNI star. Transient responses of m/z = 44 (C₃H₈ and CO₂) and m/z = 44, 43 (C₃H₈) over as-prepared catalysts was tested by an on-line mass spectrometer against a pulsed ³⁵ introduction of C₃H₈ under steady flow of mixture gas (10% CO₂)

and 90% Ar). Reaction conditions: catalyst = 100 mg; CO_2 and Ar carrier = 30 mlmin⁻¹; $C_3H_8 = 1$ ml; furnace temperature = 550°C. Thermogravimetric analysis (TGA) was conducted on a

Rigaku TG analyzer to determine the amount of coke deposited 40 on the catalyst after the reaction. 10 mg of sample was heated from room temperature to 800 °C at a heating rate of 10 °C/min in flowing air.

2.3 Catalyst evaluation

The catalyst test was carried out in a horizontal quartz tube fixed-⁴⁵ bed reactor. Reaction conditions: T = 550 °C; P = 100 kPa; $m_{cat} = 150$ mg; the feed gas mixture $C_3H_8/CO_2/N_2$ with the molar ratio of 1:3:27; total flow rate = 15 cm³·min⁻¹.

The products were analysed by off-line gas chromatograph (HUAAI GC 9560) equipped with a FID with Al₂O₃ packed ⁵⁰ column, and offline gas chromatograph (East & West GC 4000A) equipped with a thermal conductivity detector (TCD) with carbon molecular sieves packed column, respectively. The propane conversion and propylene selectivity were calculated using the following eqs (1) and (2).

⁵⁵ Where $X_{propane}$ is the conversion of propane, $S_{propylene}$ is the selectivity of propylene, $N_{propane,in}$ and $N_{propane,out}$ are the numbers

$$X_{propane} = \frac{(N_{propane,in} - N_{propane,out})}{N_{propane,in}} \times 100\%$$
(1)

$$S_{propylene} = \frac{N_{propylene}}{N_{propane,in} - N_{propane,out}} \times 100\%$$
(2)

60 of moles of propane in the inlet and outlet gas phases, respectively, and N_{propylene,out} is the number of moles of product propylene.

Regeneration conditions: T = 600 °C; air or pure CO₂ (99.99%); flow rate = 30 ml/min; treatment time = 10 h.

65 3. Results and discussion

3.1 Catalyst test

The conversion of propane and the selectivity of propylene over these as-prepared samples as a function of time on stream are shown in Fig. 1. Compared with single Al₂O₃, the activity of 70 Ga₂O₃-containg catalysts are remarkably superior for propane dehydrogenation (Fig. 1A), indicating that the presence of Ga

species is necessary to generate active sites for propane dehydrogenation.³⁵ Especially on GA-HS, the initial propane conversion is the highest (35.2%), which is much higher than that ⁷⁵ on Ga₂O₃ (5.7%), GA-GM (8.7%) and GA-CP (26.2%). From

Fig. 1B, it is noticeable that propylene selectivity over these Ga_2O_3 -containing catalysts achieve to about 95.0%, which are obviously higher than that on single Al_2O_3 (only 73.2%). Propylene selectivity over Ga_2O_3 and GA-GM decrease by 13.7% and 26.5% reconcisions of the results of the total of the results of the resul

⁸⁰ and 26.5 % respectively after 9 h reaction, while that over GA-HS and GA-CP almost remain unchanged during the running period accompanied by the decline of propane conversion. Seemingly, the propylene selectivity over GA-HS is slightly higher than that over GA-CP. These test results suggest that the

activities of Ga₂O₃-containing catalysts are strongly affected by the preparation method and treatment process. And our adopted hydrothermal synthesis method is remarkably favourable for preparing the catalyst for efficient dehydrogenation of propane, in comparison with the grind-mixture method or coprecipitation ⁹⁰ method. In addition, pure Ga₂O₃ (G-HS) and Al₂O₃ (A-HS) are prepared using hydrothermal synthesis method in comparison

with GA-HS. The initial propane conversions on G-HS and A-HS are 21.4% and 0.8% (Fig. S1a) respectively, much lower than that on GA-HS, implying that single Ga₂O₃ or Al₂O₃ component is ⁹⁵ indifferent for propane dehydrogenation but their synergistic

effect is active due to forming special structure. Besides, the rapid decreases of propylene selectivity on G-HS and A-HS (Fig. S1b) are seen with increase of time on stream in comparison with GA-HS. Moreover, Ga₂O₃-Al₂O₃ materials with different Ga/Al molar ¹⁰⁰ ratios (1:1 and 2:1) are also investigated. From evaluation results of these catalysts, it's found that the conversions of propane on

of these catalysts, it's found that the conversions of propane on the Ga₂O₃-Al₂O₃ catalysts are enhanced with the increase of Ga/Al molar ratio (Fig. S1a). Wherein, the Ga₂O₃-Al₂O₃ prepared using hydrothermal synthesis method still shows the superior activity for propane dehydrogenation in the presence of CO₂ to those catalysts prepared using grind-mixture method and coprecipitation method with the same Ga/Al molar ratio. The propylene selectivity over the hydrothermally prepared catalyst achieves to about 95.0 % during the whole test period like the 110 coprecipitated-prepared catalyst (Fig. S1b), which is higher than



Fig. 1 Propane conversion (A) and selectivity of propylene (B) as a ⁵ function of time on stream for as-prepared samples. Reaction conditions: T = 550 °C; P = 100 kPa; m_{cat} = 150 mg; the feed gas mixture $C_3H_8/CO_2/N_2$ with the molar ratio of 1:3:27; total flow rate = 15 cm³·min⁻¹.



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Fig. 2 TG (A) and DTA (B) profiles of spent Ga-containing catalysts.

In order to study the effect of CO₂ on this reaction, the catalytic tests without CO₂ are performed over these Ga₂O₃-Al₂O₃ 15 catalysts for comparison (Fig. S2 and Table S1). The initial conversions of propane on these Ga2O3-Al2O3 catalysts without CO₂ are higher than that with CO₂, indicating that the presence of carbon dioxide is not positive to promote the dehydrogenation of propane as expected. Xu et al.37 considered that the negative 20 effect was been attributed to the greatly reduced propane adsorption capacity due to the competition of CO₂. However, compared with catalytic tests in presence of CO₂, rapid deactivation of these Ga₂O₃-Al₂O₃ catalysts in the absence of CO₂ is observed. And propane conversions on these Ga₂O₃-Al₂O₃ 25 catalysts testing in presence of CO₂ are higher than that in the absence of CO₂ after 9 h on stream. It can be indicated that the presence of CO₂ is beneficial for improving durability of the catalysts. The enhanced stability of these Ga2O3-Al2O3 catalysts in the presence of CO₂ may be due to their low coking ³⁰ tendency.¹² In addition, the primary product (propylene) and byproducts (methane, ethylene, ethane, etc.) are formed during the dehydrogenation process of propane regardless of the presence of CO₂. However, it is worthy to note that the selectivity to byproducts over these Ga₂O₃-Al₂O₃ catalysts in the presence of CO₂ $_{35}$ is lower than that in the absence of CO₂. It is thought that CO₂ as a mild oxidant can promote the dehydrogenation of propane preferentially and weaken the cracking and hydrocracking reactions somewhat, thereby increasing the selectivity of target product propylene compared with that in absence of CO₂. With 40 the observation of higher conversion of CO₂ and lower molar ratio H₂/CO over GA-HS (Table S1), it can be further confirmed that GA-HS has superior activity to GA-GM and GA-CP in the present reaction. The catalytic tests of GA-HS after regeneration with air or CO_2 are performed (Fig. S3). The comparative results 45 of regeneration with O₂ and CO₂ indicate that both agents are effective in coke removing. But propane conversion and propylene selectivity on regenerated GA-HS with CO₂ after 9h reaction on stream are much lower than that with air, implying that the CO₂ can partly remove the coke through Boudouard 50 reaction. 37

Considering the distinction of test conditions (such as reaction temperature, GHSV and CO₂/C₃H₈ molar ratio of feed gas mixture, etc.), it is difficult to make a certain conclusion that which preparation method is more preferential by comparing the 55 activities of the Ga₂O₃-containing catalysts prepared by different researchers. But it is widely accepted that the presence of Lewis acid sites related to Ga³⁺ ions in tetrahedral sites, which is obtained through special treatment process such as hydrothermal synthesis, is favourable for propane dehydrogenation. However, 60 propane conversion and propylene selectivity over GA-HS are higher than that over these catalysts prepared using grind-mixture method or coprecipitation method at the same test conditions, indicating that the hydrothermal synthesis can improve the activity of Ga₂O₃-Al₂O₃ catalysts greatly. In this work, we focus 65 on the effect of preparation method on the activity of Ga₂O₃-Al₂O₃ catalysts for DHP-CO₂.

Propane conversions over these Ga_2O_3 -containing samples all decrease as a function of reaction time. Wherein, it is thought that this gradual deactivation of the catalysts is caused by the coke

deposition on the surface of these catalysts.^{25, 36} Based on that, coke deposition on the spent Ga-containing samples is quantified by TG-DTA as show in Fig. 2A. The weight loss of these spent samples decreases in the order: GA-HS > GA-CP > GA-GM > 5 Ga₂O₃. Spent GA-HS displays maximum weight loss compared with the Ga₂O₃-Al₂O₃ catalysts prepared using grind-mixture method or coprecipitation method, demonstrating its high coke performance. Published work^{19, 30} reported that the high catalytic performance of Ga-containing materials is attributed to the 10 surface gallium sites with Lewis acidity, which are also the coke deposition sites. For the present catalysts, GA-HS should possess more Lewis acid sites than the others based on its relatively good performance (as shown in Fig. 1A). That implies that there are more coke deposition sites existed on GA-HS. Moreover, the 15 initial conversion of propane (Fig. S2) and the initial selectivity of propylene (Table S1) over these Ga₂O₃-Al₂O₃ catalysts in the absence of CO₂ are much higher. This result suggests that the concentration of propylene in the absence of CO₂ in the initial step is also high. Because the propylene is more reactive than 20 propane, its higher concentration in reaction zone leads probably to higher coke amount, which also contributes to fast deactivation of catalyst in the dehydrogenation of propane in terms of substrates-products reactivity.^{17, 30} Thus, the coke is easily formed on GA-HS catalyst during DHP-CO₂ process due to its high 25 activity. In addition, the coke also has significant effects on the durability of these catalysts. As our observation, the propane conversion decrease dramatically with increase of time

30 Table 1 Textural properties of different samples

	S ^a _{BET}	S ^a micro	Sext	V ^b total	V ^b _{micro}	V _{ext}	
Sample	(m^2/g)	(m^2/g)	(m^2/g)	(cm^3/g)	(cm^3/g)	(cm^3/g)	
Al ₂ O ₃	68.8	15.7	53.1	0.075	0.007	0.068	
Ga_2O_3	29.2	5.9	23.3	0.129	0.003	0.126	
GA-GM	39.9	13.7	26.2	0.076	0.001	0.075	
GA-CP	220	32.0	188	0.438	0.013	0.425	
GA-HS	234	22.0	212	0.730	0.008	0.722	
^a determined by t-method: ^b determined by Volume adsorbed at $p/p^0=0.9^{\circ}$							



Fig. 3 Pore size distributions for different catalysts.

on stream. In addition, DTA profiles of the spent Ga-containing (Fig. 2B) show that both spent GA-GM and spent Ga₂O₃ only display one peak at 460 °C and 426 °C respectively, 40 corresponding to one type of carbon species. But the spent GA-CP shows two peaks at 454 °C and 479 °C assigned to two different types of carbon species. Spent GA-HS displays a similar DTA profile to the spent GA-CP, but with higher amounts of carbon species. Nevertheless, it deserves further study to 45 understand the details about the mechanism of formation of different carbon species.

3.2 Catalyst composition and textural properties

The pore volume, pore size and BET surface areas (S_{BET}) of different catalysts are obtained based on sorption isotherms of N₂ 50 condensation at 77 K. N2-sorption isotherms of these catalysts (Fig. S4) are a type IV with a steep increase around $P/P_0 = 0.4$, indicating that these samples belong to typical mesoporous materials.^{41, 42} From the profiles of pore size distributions in Fig. 3, it can be seen that GA-GM and GA-CP have a very narrow 55 pore size distribution with average pore diameter 7.6 nm and 7.9 nm respectively, while GA-HS has a broad pore size distribution with average pore diameter 12.5 nm. This suggests that special pore structure can be produced after the hydrothermal treatment. The BET surface area and total volumes of the catalysts are 60 calculated and the results are shown in Table 1. The BET surface area and total volumes of GA-HS are 234 m²/g and 0.730 cm³/g respectively, higher than that of GA-GM, GA-CP, pure Ga₂O₃ and pure Al₂O₃. In combination with the above test results,

65 Table 2 Textural properties of different spent and regenerated Ga2O3-Al₂O₃ catalysts

Sample	S^{a}_{BET} (m^{2}/g)	S^{a}_{micro} (m ² /g)	S_{ext} (m^2/g)	V^{b}_{total} (cm ³ /g)	V^{b}_{micro} (cm ³ /g)	V_{ext} (cm ³ /g)	D _{pore} (nm)
GA-GM	73.0	5.7	67.3	0.089	0.003	0.086	4.9
	(74.6)	(5.5)	(69.1)	(0.107)	(0.002)	(0.105)	(5.7)
GA-CP	123.8	12.2	111.6	0.141	0.008	0.133	4.5
	(161.4)	(8.4)	(153.0)	(0.235)	(0.002)	(0.233)	(5.8)
GA-HS	160.0	3.4	156.6	0.187	0.004	0.183	4.6
	(190.7)	(4.3)	(186.4)	(0.322)	(0.004)	(0.318)	(6.7)

^a determined by t-method; ^b determined by Volume adsorbed at p/p⁰=0.97

The value outside and inside the bracket are the data of the BET surface 70 areas, pore volumes and pore diameter obtained after reaction and after one-round regeneration with air (30 ml/ min) respectively.

Table 3 Compositions and numbers of acid sites in as-prepared catalysts

	Ga/Al molar ratio		Ga ^{Te}	$Ga^{T}_{total}{}^{d}$	NH ₃ desorbed ^e
Sample	Bulk ^a	Surface ^b	(%)	(%)	(mmol g ⁻¹ cat)
Al ₂ O ₃	/	/	/	/	0.079
Ga ₂ O ₃	/	/	9.5	9.5	0.047
GA-GM	0.587	0.505	37.7	13.9	0.073
GA-CP	0.536	0.920	78.3	27.3	0.141
GA-HS	0.576	1.11	85.5	31.2	0.168

^a determined by ICP-AES method; ^b determined by XPS; ^c determined by ⁷¹Ga MAS NMR; ^d Ga total (IV) % = $n_{Ga}/(n_{Ga} + n_{Al}) \ge Ga$ (IV) %, $n_{Ga}/(n_{Ga} + n_{Al})$ is the bulk molar ratio; e determined by NH3-TPD.



Fig. 4. XRD profiles of as-prepared samples (a) Ga_2O_3 ; (b) GA-GM; (c) GA-CP; (d) GA-HS; (e) Al_2O_3 .

⁵ it is thought that active Ga species can be more easily dipersed on GA-HS due to its high BET surface and volumes than that of GA-GM and GA-CP, thereby leading to its good performance probably. Moreover, the higher micropore surface area and micropore volumes of GA-CP than that of GA-HS and GA-GM
¹⁰ means that using a coprecipitation method can lead to the preferential formation of micropores over GA-CP than other catalysts. Based on the larger number of mes- and macro-pores in GA-HS than GA-CP and GA-GM, the conclusion can be made that hydrothermal synthesis promotes the formation of mes- and ¹⁵ macro-pores over the Ga₂O₃-Al₂O₃ catalyst, but the coprecipitation method is in favor of formation of micropores.

To clarify the thermal stability of the catalyst prepared by hydrothermal method, the textural properties of the samples after DHP-CO₂ test and regeneration with air have been characterized ²⁰ by low N₂ adsorption and the data is listed in Table 2. Compared with the fresh samples, the spent GA-CP and spent GA-HS both show obvious decrease in the S_{BET} (decrease by 96.2 m²/g and 74.0 m²/g) and pore volume (decrease by 0.297 m³/g and 0.543 m³/g) respectively, whereas the spent GA-GM shows some ²⁵ increase in the S_{BET} and pore volume (incease by 33.1 m²/g and 0.014 m³/g) due to cumuli of coke deposition. After regeneration with air, pores of these spent Ga₂O₃-Al₂O₃ catalysts are recovered partly. And the regenerated GA-HS still shows the highest S_{BET} and pore volume among these regenerated samples, indicating ³⁰ that the hydrothermal synthesis method is superior to other preparation methods in this work.

Fig. 4 illustrates the XRD patterns of these Ga_2O_3 - Al_2O_3 catalysts, along with simple Ga_2O_3 and Al_2O_3 . The diffraction lines of the as-prepared samples are very broad, demonstrating a

- ³⁵ low crystallinity of all the samples. This low crystallinity is a common feature of metastable γ -variety of both alumina and gallia polymorphs.¹² The as-prepared Ga₂O₃ reveals the typical characteristics of γ -Ga₂O₃ inferred from the 2 θ angles (30.8°, 36.2° and 64.2° in curve a) of diffraction peak, while simple
- ⁴⁰ Al₂O₃ suggests the typical characteristics of γ -Al₂O₃ based on the 2θ angles (45.4°, 60.3° and 67.1° in curve e) of the diffraction peak. GA-GM closely resembles γ -Ga₂O₃ and γ -Al₂O₃ in the light of diffraction maxima (curve b), indicating that no new structures



Fig. 5 ^{71}Ga MAS NMR profiles of different catalysts. (a) GA-GM; (b) GA-CP; (c) GA-HS.



Fig. 6 Ga 3d XPS (A) and Ga 2p_{1/2} XPS (B) profiles of different catalysts. ⁵⁰ (a) GA-GM; (b) GA-CP; (c) GA-HS.

are formed in physical mixture process. Yet GA-CP and GA-HS don't exhibit typical characteristics of simple γ -Ga₂O₃ and/or γ -Al₂O₃ like GA-GM. d₍₄₄₀₎ spacing corresponds to cubic lattice parameter a₀, which can be used to distinguish the cubic spinelsystem to the cubic spineltype structure (gallia-alumina solid solution) by the location of (440) peak.⁴⁰ It can be seen that the (440) peaks of γ -Ga₂O₃ and γ -Al₂O₃ are located at 64.2° and 67.1° respectively. The (440) peaks of GA-CP and GA-HS lie between that of γ -Ga₂O₃ and γ -Al₂O₃, indicating that the cubic spinel-type structures are formed on GA-60 CP and GA-HS.⁴³ In comparison with GA-CP, the (440) peak of

GA-HS shifts to high 2θ angle due to preparation method. This

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(5)

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suggests that different structure presents on GA-CP and GA-HS in despite of the presence of similar cubic spinel-type structures on these two catalysts, which results in their activity differences for propane dehydrogenation.

5 3.3 Coordination state and oxidation state of Ga

To reflect the coordination state of Ga^{3+} ion, the ⁷¹Ga MAS NMR chemical shift measurements are conducted and the spectra of different catalysts are shown in Fig. 5. The two asymmetric bands within -100 ppm ~ 300 ppm are assigned to tetrahedral Ga (Ga^T)

10 ions and octahedral Ga (Ga^O) ions, respectively.^{14, 40, 44-46} Peak deconvolution of the NMR Ga^T and Ga^O bands are also done to provide more information about the Ga distribution (among tetrahedral and octahedral sites) in the structure of these catalysts. The deconvoluted results in Table 3 suggest that most of Ga ions 15 in GA-GM and Ga₂O₃ occupy octahedral Ga⁰ sites while that in GA-CP and GA-HS are mainly located at tetrahedral Ga^T sites. Especially for GA-HS, the Ga^T ions percent achieves to 85.5%. It indicates that hydrothermal synthesis method promotes the formation of tetrahedral Ga^T ions. Besides, the content of total ²⁰ Ga^T ions is also calculated in combination with bulk content of the Ga obtained by ICP-AES. The results show that the content of total Ga^T ions of GA-HS is higher than GA-GM and GA-CP. Already published research^{36, 37} indicated that the lowcoordinated Ga^T cations contributed to the activity of Ga₂O₃-25 containg catalysts for DHP-CO2. And it is consistent with our results that the content of Ga^T cations has a positive relationship

with activity of Ga2O3-containg catalysts for propane

dehydrogenation. Propane can heterolytically dissociate on lowcoordinated surface Ga³⁺ sites in gallium oxide, forming gallium ³⁰ hydride and gallium alkoxide species as step (3), and the alkoxides then decompose further to the dehydrogenation products as step (4) and (5) as follows:

$$\begin{array}{c} H^{-} C_{3}H_{7}^{+} \\ Ga^{3+}-O^{2}-M^{3+}+C_{3}H_{8} \rightarrow Ga^{3+}-O^{2-}-M^{3+} (M = Ga, Al) \quad (3) \\ s H^{-} C_{3}H_{7}^{+} H^{-} H^{+} \\ Ga^{3+}-O^{2}-M^{3+}+C_{3}H_{8} \rightarrow Ga^{3+}-O^{2-}-M^{3+}+C_{3}H_{6} \qquad (4) \\ and \\ H^{-} H^{+} \end{array}$$

 $Ga^{3+}-O^2-M^{3+} \rightarrow Ga^{3+}-O^{2-}-M^{3+}+H_2$

⁴⁰ When CO_2 is introduced into the propane dehydrogenation reaction, chemisorbed H₂ generates from the step (5) can be removed via an alternative route as step (6):

$$\begin{array}{c} H^{-} & H^{-} \\ Ga^{3+} - O^{2} - M^{3+} + CO_{2} \rightarrow Ga^{3+} - O^{2-} - M^{3+} + CO + H_{2}O \quad (6) \end{array}$$

It's apparent that the more low-coordinated surface Ga³⁺ sites are obtained in the Ga₂O₃-containg catalysts, the better catalytic activity in propane dehydrogenation is. Apart from that, the coordination state of the Al³⁺ ion is also investigated by ²⁷Al ⁵⁰ MAS NMR and the results are shown in Fig. S5 and the percentage of Al³⁺ ions are listed in Table S2. The results suggest that the percentage of Al³⁺ ion in GA-HS is higher than that in GA-GM and GA-CP, indicating that hydrothermal synthesis



Fig. 7 TEM images of different as-prepared catalysts: (a) Al₂O₃; (b) Ga₂O₃; (c) GA-GM; (d) GA-CP; (e, f) GA-HS.

promotes the formation of more tetrahedral Al^{T} ions as well as tetrahedral Ga^{T} ions.

XPS is an effective technique to characterize the surface 5 situation of catalysts.⁴⁷⁻⁵² Oxidation states and quantity of the elements that are present within the top 1-12 nm of the sample surface can be obtained by this technique. The surface Ga/Al ratios measured by XPS and the bulk Ga/Al ratios determined by ICP-AES are shown in Table 3. The surface Ga/Al ratio of GA-10 GM is lower than bulk Ga/Al ratio, while the surface Ga/Al ratios of GA-CP and GA-HS are higher than their bulk Ga/Al ratios. This indicates that the coprecipitation synthesis and hydrothermal synthesis could make more Ga species expose on the surface of Ga₂O₃-Al₂O₃ catalysts. This is also verified by SEM-EDS results 15 (Fig. S6), which show that the surfaces of GA-CP and GA-HS are remarkably enriched in Ga, compared with GA-GM. The Ga 3d and Ga 2p_{1/2} XPS spectra of these catalysts are displayed in Fig. 6. From the deconvoluted spectra on the Ga 3d region (Fig. 6A), the observation is that only two peaks appear in the spectra of GA-20 GM and GA-CP at about 24.1 and 20.6 eV respectively, which are assigned to O2s and Ga³⁺ 3d bands.⁵³ As for GA-HS, a new and additional low-energy peak at 19.6 eV is found, which can be attributed to the presence of Ga^{δ^+} species ($\delta^{< 2}$),^{21, 54} suggesting that the reduced Ga species are probably generated by the $_{25}$ hydrothermal synthesis. This can be further verified by Ga $2p_{1/2}$ XPS spectra (Fig. 6B). It can be seen that the GA-CP and GA-GM only show one oxidation state, and Ga $2p_{1/2}$ binding energy (BE) value for GA-CP (1144.6 eV) is higher than that for GA-GM (1144.2 eV). While GA-HS show two oxidation states 30 (1144.2 eV and 1147.9 eV, respectively). It is deduced that the other Ga oxidation state (1147.9 eV) ascribed to Ga^{δ^+} species probably is formed on GA-HS, due to the surface enrichment of Ga species and generation of more low-coordinated Ga¹ species by hydrothermal treatment. The dehydrogenation of propane over 35 reducible metal oxide catalysts such as chromium and iron oxides in the presence of CO₂ has been suggested to follow a redox mechanism.⁵⁵ That is, propane is oxidized to propylene with the simultaneous reduction of metal oxide (e.g. Fe₂O₃, Cr₂O₃), and subsequently the reduced metal oxide catalyst is reoxidized by ⁴⁰ CO₂. According to the above results, Ga^{δ^+} species ($\delta^< 2$) exist in

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- ⁴⁰ CO₂. According to the above results, Ga⁻⁻ species (6< 2) exist in our prepared GA-HS and the mentioned redox mechanism is probably applicable for the present catalyst system. However, compared that the fresh catalyst, the spent GA-HS with or without CO₂ (Fig. S7A) shows two binding energy peaks in Ga ⁴⁵ 3d XPS spectra at about 24.1 eV and 20.8 eV assigned to O2s and
- $_{45}$ 3d XPS spectra at about 24.1 eV and 20.8 eV assigned to O2s and Ga³⁺ 3d bands respectively, and yet the original low-energy peak at 19.6 eV attributed to the presence of Ga^{δ+} species (δ < 2) disappears. It is deduced that these Ga^{δ+} species have been converted into Ga³⁺ species probably. This can be also further
- ⁵⁰ verified by the disappearance of binding energy peak at 1147.9 eV (ascribed to the Ga oxidation state) in Ga $2p_{1/2}$ XPS spectra (Fig. S7B) after reaction with or without CO₂. Compared with fresh GA-HS, oxidation states in the spent GA-HS with CO₂ are similar to that without CO₂, implying that the redox mechanism in
- ss which the CO_2 is taken as an oxidant is not available for the present catalyst. However, CO_2 still plays a positive role in the enhancement of dehydrogenation activity through reverse watergas shift reaction and elimination of coke by Boudouard

reaction.³⁷ The reduced gallium ions (Ga^{δ^+} species $\delta < 2$) are also ⁶⁰ thought to have high dehydrogenation efficiency. The galliumhydrogen bond can be formed on these reduced gallium ions by heterolytic hydrogen dissociation, and can be stabilized on the support surface.²¹ Therefore, dehydrogenation proceeds on the supported gallium oxide catalysts probably through a heterolytic dissociation reaction pathway instead of radox mechanism

⁶⁵ dissociation reaction pathway instead of redox mechanism. Wherein, it should be pointed out that the further work needs to be done to clarify the mechanism of conversion of $Ga^{\delta+}$ species (δ < 2) to Ga^{3+} species with and without CO₂.

3.4 Morphologies of as-prepared samples

70 In order to reveal the morphologies of these as-prepared samples, TEM is applied and the results are shown in Fig. 7. Al₂O₃ shows smooth pieces (Fig. 7a) while Ga₂O₃ takes on an irregular and segregated morphology (Fig. 7b). GA-GM as shown in Fig. 7c mainly contains two kinds of morphologies. Wherein, it is ⁷⁵ thought that they are ascribed to Ga₂O₃ and Al₂O₃ respectively, in combination with Fig. 7a, 7b. While GA-CP (Fig. 7d) just exhibits a unified distinct sponge-like morphology probably ascribed to gallia-alumina solid solution (cubic spinel-type structure) inferred from the XRD results that gallia-alumina solid ⁸⁰ solution (cubic spinel-type structure) is generated. In case of GA-HS, besides amorphous sponge-like morphology like GA-CP as shown in Fig. 7d, an additional morphology (Fig. 7e) that some pieces are covered with amorphous nanoparticles is also seen. Furthermore, some amorphous nanoparticles can embed into 85 these pieces (Fig. 7f). It's easily understandable that the distinct multiple morphologies of these samples are ascribed to their different structures, which are determined by preparation method

3.5 Acidity of the catalysts

and treatment process.

- ⁹⁰ A comparison of the DRIFT spectra in the OH stretching region for the as-prepared samples is showed in Fig. 8. The stretching band of Ga-OH groups for Ga₂O₃ and Al-OH for Al₂O₃ are located at 3650 cm⁻¹ and 3716 cm⁻¹ respectively. As for GA-GM, no any stretching bands of Al-OH groups or Ga-OH groups are
 ⁹⁵ observed but only a broad region, probably because of the formation of disordered mixture between Al₂O₃ and Ga₂O₃. GA-CP and GA-HS both show a new stretching band of special group at about 3683 cm⁻¹, which is assigned to Ga-OH or Al-OH in the cubic spinel-type structure. The appearance of the new OH group
 ¹⁰⁰ somewhat affects the acidity of catalyst. Based on that, the distribution of acidity on these different catalysts is measured by NH₃-TPD and the profiles are shown in Fig. 9. It can be seen that there is only one NH₃ desorption peak over these catalysts. The
- desorption peak on GA-HS shows an obvious shift to higher ¹⁰⁵ temperature (315 °C) in comparison with that on GA-GM (284 °C) and GA-CP (303 °C), meaning that the acidity strength of the GA-HS is enhanced facilely via the hydrothermal synthesis and the medium-strong Lewis acid sites are generated on the catalyst accordingly. Moreover, the increased number of Lewis ¹¹⁰ acid sites over GA-HS, in comparison of GA-CP and GA-GM
- (Table 3), implies that the hydrothermal synthesis promotes the formation of medium-strong Lewis acid sites. It has been proved that the dehydrogenation of propane proceeded mainly on the



Fig. 8 DRIFT spectra of as-prepared samples in the OH stretching region were recorded after treating the catalyst *in-situ* at 300 °C for 1 h with a s flow of argon. (a) Ga₂O₃; (b) GA-GM; (c) GA-CP; (d) GA-HS; (e) Al₂O₃.



Fig. 9 (A) NH₃-TPD profiles of different Ga_2O_3 -Al₂O₃ catalysts: (a) GA-GM; (b) GA-CP; (c) GA-HS.



10 Fig. 10 Py-FTIR spectra of different Ga₂O₃-Al₂O₃ catalysts: (a) GA-GM; (b) GA-CP; (c) GA-HS.



Fig. 11 Transient responses of m/z = 44 (C_3H_8 and CO_2) over as-prepared catalysts against a pulsed introduction of C_3H_8 under steady flow of ¹⁵ mixture gas (10%CO₂ and 90%Ar). Reaction conditions: catalyst = 100 mg; CO₂ and Ar carrier = 30 mlmin⁻¹; $C_3H_8 = 1$ ml; furnace temperature = 550°C. (a) GA-GM; (b) GA-CP; (c) GA-HS.

Lewis acid sites related to low-coordinated Ga³⁺ ions on Ga₂O₃containing catalysts, which affected intensively their activities for ²⁰ dehydrogenation of propane.^{12, 56} It's apparently plausible that large amount of Lewis acid sites over GA-HS play a key role in improving the catalytic performance for propane dehydrogenation.

Apart from the acidity number and acidity strength of active sites over these catalysts, the acidity type also contributes to their 25 catalytic performance for propane dehydrogenation. Based on that, FTIR spectra of pyridine adsorption on different catalysts are recorded to identify the Brønsted acid sites and Lewis acid sites, and the results are shown in Fig. 10. two peaks, at 1458 cm and 1620 cm⁻¹ respectively, appear over all these catalysts, 30 which are assigned to Lewis acid sites.^{44, 57} That's to say, only Lewis acid sites exist on these Ga₂O₃-Al₂O₃ catalysts. In view of NH₃-TPD profiles, it is deduced that the desorbed NH₃ arise from Lewis acid sites. And these Lewis acid sites are related to coordinately unsaturated Ga³⁺ ions in the tetrahedral position.⁵⁷ 35 It's apparent that GA-HS possesses more Ga³⁺ ions in the tetrahedral sites than GA-GM and GA-CP because of more number of Lewis acid sites on GA-HS inferred from by NH₃-TPD, thereby showing better catalytic performance substantially. This

result is consistent with the NMR results. ⁴⁰ Chen *et al.*^{11, 12} reported that surface acidity (specifically Lewis acid sites density of surface) on the Ga₂O₃–Al₂O₃ catalysts is crucial to obtain high activity and stability in propane dehydrogenation. Wherein, the surface acidity is attributed to the surface tetrahedral Ga³⁺ ions. Therefore, the investigation to ⁴⁵ surface tetrahedral Ga³⁺ sites is helpful to understand the propane dehydrogenation in-deep. As proposed, propane activation firstly

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proceeds on these low-coordinated Ga³⁺ cations, forming propyl-Ga species, and then the dehydrogenation products are generated by subsequent decomposition of the resulting propyl-Ga species. In our work, a positive correlation between the number of Ga ⁵ species in tetrahedral sites and the number of surface Lewis acid sites on GA-HS further verifies the previous work.¹²

3.6 Pulsed reaction

To gain more insight into the mechanism of DHP-CO₂ over the different catalysts, a pulsed reaction technique is used to measure ¹⁰ the activities of these catalysts.¹³ The transient responses over asprepared catalysts against a pulsed introduction of C_3H_8 at 550°C under steady flow of mixture gas (10% CO₂ and 90% Ar) are tested by an on-line mass spectrometer as well as the contrast tests, and the results are shown in Fig. 11. When C_3H_8 is pulsely ¹⁵ introduced under steady flow of pure Ar, similar narrow and positive peaks with the transient response of m/z= 44 (C_3H_8) over all these catalysts (Fig. S8) can be seen. Besides, the transient response of m/z= 43 determined as C_3H_8 also can be noticed. ^{58, 59} When steady flow is introduced with 10% CO₂, the peak ²⁰ responses of m/z = 43 and m/z = 44 over theses catalysts are

- obviously different. The transient response of m/z= 43 over GA-GM, GA-CP and GA-HS are all similar and present as narrow peaks (Fig. S9), suggesting that C_3H_8 is detected over these catalysts. In case of the responses of m/z = 44 over GA-HS, the ²⁵ inverted peaks apparently indicate that the introduced C_3H_8 and CO_2 has been consumed greatly (Fig. 11c). Whereas, the narrow and positive peaks of GA-CP imply that the remarkable amount of C_3H_8 feedstock is still reserved (Fig. 11b). The largest broad
- and positive peaks of the transient response (m/z = 44) over GA-³⁰ GM (Fig. 11a), indicate the weak conversion of C_3H_8 . Conclusively, the above results suggest that activity of GA-HS for DHP-CO₂ is higher than that over other catalysts, which agrees with the previous test results.
- Reported work⁶⁰⁻⁶³ has shown that hydrothermal conditions 35 (generated self-pressure, hydrothermal temperature and time) had great influence on the crystallization and formation process of the catalysts. In this work, the characterization data suggested that hydrothermal conditions such as generated self-pressure, hydrothermal temperature and time (170 °C for 24 h) played 40 significant roles in improving the dispersion and distribution of surface gallium sites. Through the hydrothermal process, more tetrahedral Ga³⁺ sites gallium sites were exposed on the surface of GA-HS, thus contributing to formation of surface Lewis acid sites. Moreover, this hydrothermal treatment is also favorable for 45 improving surface area and increasing pore volume of the catalyst. It's the superior structure and physical properties obtained by hydrothermal synthesis that ultimately result in high activity for dehydrogenation of propane. Therefore, it can be concluded apparently that hydrothermal synthesis is quite an 50 effective method to obtain an efficient Ga₂O₃-Al₂O₃ catalyst for
- so effective method to obtain an efficient Ga₂O₃-Al₂O₃ catalyst for propane dehydrogenation.

4. Conclusion remarks

A Ga₂O₃–Al₂O₃ catalyst (GA-HS) prepared using hydrothermal synthesis method showed prominent activity for the DHP-CO₂. ⁵⁵ The highest propane conversion achieved on GA-HS catalyst was 35.2%, which was much higher than that of GA-GM (8.7%)

prepared using grind-mixture method and GA-CP (26.2%) prepared using coprecipitation method. Furthermore, the propylene selectivity over GA-HS was highest among these 60 catalysts during the whole reaction time. On the other hand, propane conversion and propylene selectivity as a function of time on stream on regenerated GA-HS with CO2 are some low in comparison with that on fresh GA-HS, implying that the coke can be partly eliminated with CO₂ through Boudouard reaction. 65 Besides, the introduction of CO₂ to this reaction system improved durability of the catalysts in spite of the decreased initial conversions of propane on these Ga₂O₃-Al₂O₃ catalysts. Characterization results such as BET, XPS, etc. suggested that hydrothermal conditions such as generated self-pressure, 70 hydrothermal temperature and time (170 °C for 24 h) played significant roles in improving the dispersion and distribution of surface gallium sites. This process made more tetrahedral Ga³⁺ sites expose on the surface of GA-HS, which contributed to formation of surface Lewis acid sites. Moreover, the 75 hydrothermal treatment is favorable for improving surface area and increasing pore volume of the catalyst. The texture of GA-HS was largely recovered with air regeneration even after 9 h reaction time well. Higher surface area and larger amount of tetrahedral Ga ions (Ga³⁺ and probably Ga^{δ^+}) related to strong ⁸⁰ Lewis acid sites were responsible for the superior activity of GA-HS catalyst. The correlative work about generation and effect of Ga^{δ^+} ions are still on-going.

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90 Notes and references

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Hydrothermal synthesized Ga₂O₃-Al₂O₃ catalysts showed superior activity for dehydrogenation of propane in the presence of carbon dioxide