Support Effect of Ga-Based Catalysts in the CO\textsubscript{2}-Assisted Oxidative Dehydrogenation of Propane

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Abstract: Carbon dioxide (CO\textsubscript{2}) assisted oxidative dehydrogenation of propane over Ga-modified catalysts is highly sensitive to the identity of support, but the underlying cause of support effects has not been well established. In this article, SSZ-13, SSZ-39, ZSM-5, silica and γ-Al\textsubscript{2}O\textsubscript{3} were used to load Ga species by incipient wet impregnation. The structure, textural properties, acidity of the Ga-based catalysts and the process of CO\textsubscript{2}-assisted oxidative dehydrogenation of propane were examined by X-ray diffraction (XRD), nitrogen physisorption (N\textsubscript{2} physisorption), ammonia temperature-programmed desorption (NH\textsubscript{3}-TPD), pyridine chemisorbed Fourier transform infrared spectra (Py-FTIR), OH-FTIR and in situ FTIR. Evaluation of the catalytic performance combined with detailed catalyst characterization suggests that their dehydrogenation activity is positively associated with the number of acid sites in middle strength, confirming that the Lewis acid sites generated by Ga cations are the active species in the reaction. Ga/Na-SSZ-39(9) also has feasible acidic strength and a unique channel structure, which is conducive to the dissociative adsorption of propane and desorption of olefins. The Ga/Na-SSZ-39(9) catalysts showed superior olefins selectivity and catalytic stability at 600 °C compared to any other catalysts. This approach to quantifying support acid strength, and channel structure and applying it as a key catalytic descriptor of support effects is a useful tool to enable the rational design of next-generation CO\textsubscript{2}-assisted oxidative dehydrogenation catalysts.

Keywords: support effect; gallium-based catalysts; CO\textsubscript{2}-assisted oxidative dehydrogenation; carbon dioxide

1. Introduction

The continuous increase in human demand for energy over the centuries and the growing industrial activity have led to the emission of large amounts of CO\textsubscript{2} [1,2], a gas with a “greenhouse effect” that serves to absorb infrared rays from solar radiation and thus maintain the temperature of the Earth’s surface. Statistics point to a rise in atmospheric CO\textsubscript{2} levels over the last 120 years from 280 ppm in 1900 to 419 ppm in 2019, a dramatic increase of nearly 50%. This has exerted a profoundly negative influence on the ecology of the planet on which mankind depends nowadays and has caused climate challenges such as global warming. Facing this thorny issue, researchers have been working on advanced materials that can capture and store CO\textsubscript{2} in the atmosphere and efficiently catalyze the reaction of CO\textsubscript{2} with other molecules to produce high value-added chemical materials [3].

In recent decades, the dehydrogenation of short-chain alkanes has been widely reported for its high efficiency in manufacturing light olefins such as ethylene and propylene [4–9]. Ethylene and propylene, as the crucial platform materials in the petrochemical industry, are extensively used to produce a large number of chemicals, and their annual...
global production is 160 and 110 megatons respectively [10–12]. However, with the rapid consumption of fossil energy, conventional production methods of light olefins via steam cracking of naphtha and gasoline can any longer meet the mounting demand [13]. As advances in shale gas technology have made shale gas an abundant and accessible resource, therefore, direct dehydrogenation of short-chain alkanes such as ethane and propane, which account for up to 15% of shale gas, has been widely favored for the production of light olefins [14,15]. Yet due to the thermodynamic limitations of the process, it often needs to be carried out at higher temperatures increasing the energy cost, and the commonly used catalysts for the reaction are Pt-based and Cr-based catalysts, which are environmentally unfriendly or expensive [13]. Recently, some environmentally friendly and non-noble metal-based catalysts, such as Al₂O₃ loaded with Ni₃Ga nanoparticles, Ga-modified γ-Al₂O₃ and Fe-containing MFI siliceous zeolite have also been used in direct dehydrogenation of alkanes and have demonstrated excellent performance, however, these studies are also still at the stage of laboratory research and are still a long way from practical applications [16–18].

Although oxidative dehydrogenation using oxygen as an oxidant can greatly improve the stability of the reaction, the oxidation of oxygen is too strong, resulting in the deep oxidation of propane. Hence, introducing oxidants especially CO₂, etc., into the reaction can break the thermodynamic restraint of the reaction and thus reduce the operating temperature, in addition, this can also consume the greenhouse gas CO₂, thus receiving widespread attention [9,11,19–22].

In recent years, Ga-based catalysts have attracted considerable attention for their enhancement of dehydrogenation activity [22–39]. The dehydrogenation reaction is generally considered to be catalyzed by the synergistic effects of metal sites and support. Moreover, the types and properties of the supports are extremely important, which had great influences on Ga species location, properties and unclear relationship on the structure-performance relationship. Ga-modified zeolites, especially ZSM-5 with tunable acidity, have been extensively investigated for light alkane dehydrogenation. Recently, the zeolite with chabazite (CHA) structure, an eight-membered ring zeolite, has been favorable to light alkane dehydrogenation reactions [6,40,41]. However, considering that the pore size and structure of CHA are different from that of ZSM-5 zeolite, it is uncertain whether the same types of Ga species are present in CHA. While Ga₂O₃ deactivates quickly, recent studies have shown that Ga₂O₃ on various oxide supports can be more stable and active. In particular, Al₂O₃-supported Ga catalysts have displayed improved selectivity [20,42,43].

Therefore, in this work, incipient wetness was adopted to prepare a series of Ga-modified zeolites, SiO₂ and Al₂O₃ for CO₂-assisted oxidative dehydrogenation of propane. Results showed that the zeolite catalysts possess outstanding performance in CO₂-assisted oxidative dehydrogenation of propane. In zeolites, the performance of zeolites in catalytic reactions was greatly dependent on the topological structure of the material. In order to gain insight into the catalysis of Ga-based zeolite catalysts, multiple characterization methods including XRD, N₂-physisorption, NH₃-TPD, OH-FTIR, Py-IR and in situ FT-IR were applied to catalysts and CO₂-assisted oxidative dehydrogenation of propane studies. Due to the unique channel structure and the proper amount of acid sites of medium-strong strength that can effectively confine CO₂, the Ga/Na-SSZ-39(9) catalysts showed superior olefins selectivity and catalytic stability at 600 °C compared to any other catalysts, suppressing any side reaction. In addition, CO₂ effectively promoted surface hydrogen removal, and formic acid is proposed as an intermediate formed during the reaction detected in the effluent of in situ FT-IR.

2. Results and Discussion
2.1. The Performance of CO₂ Oxidative Dehydrogenation of Propane over Ga-Based Catalysts

According to the literature [1,12,13,15,19,20], Ga-modified zeolites with low SiO₂/Al₂O₃ ratio were beneficial for the preparation of olefins over short-chain hydrocarbon dehydrogenation. Therefore, in order to further understand the catalytic role of supports, as can
be expected, Ga-modified Na-SSZ-13(27), Na-SSZ-39(9), Na-ZSM-5(28), silica and γ-Al₂O₃ were prepared.

The catalytic performance of Ga-based catalysts was evaluated as a function of time on stream (TOS). The zeolite catalysts possessed a wonderful CO₂-assisted oxidative dehydrogenation of propane performance and in zeolites, the catalytic performance was greatly dependent on the topological structure of the material. As shown in Figures 1 and 2, the illustration, in particular, depicted the conversion and selectivity obtained over Ga/Na-ZSM-5(28) and Ga/Na-SSZ-39(9). The two catalysts were selected to estimate TOS behaviors over 120 min of reaction. As shown in Figure 1, the catalytic activities of CO₂-assisted oxidative dehydrogenation of propane on the following five different catalysts were determined, and the propane conversion was in the following order: Ga/Na-ZSM-5(28) > Ga/Na-SSZ-39(9) > Ga/Na-SSZ-13(27) > Ga/γ-Al₂O₃ > Ga/SiO₂. As mentioned above, the propane conversion of Ga/Na-ZSM-5(28) catalyst exhibited excellent catalytic performance for the conversion of propane among all the catalysts. Owing to side reactions, such as cracking, and hydrogenolysis, the yield of olefins was lower than that of Ga/Na-SSZ-39(9). In addition, the catalyst gradually deactivated with the reaction proceeding, which, combined with the TGA and ICP results (see Figure S1 and Table S1), may be due to the loss of Ga species and a partial deactivation of Ga species deposited by coke.

![Figure 1](image1.png)

**Figure 1.** (a) Propane conversion and (b) CO₂ conversion over Ga-based catalysts. Reaction conditions: m_{cat} = 0.5 g, T = 600 °C, P = 0.1 MPa, GHSV = 7200 mL g_{cat}⁻¹ h⁻¹, CO₂:C₃H₈:N₂ = 1:1:18.

![Figure 2](image2.png)

**Figure 2.** Product selectivity over Ga-based catalysts within 60 min. Reaction conditions: m_{cat} = 0.5 g, T = 600 °C, P = 0.1 MPa, GHSV = 7200 mL g_{cat}⁻¹ h⁻¹, CO₂:C₃H₈:N₂ = 1:1:18.

The Ga/Na-SSZ-39(9) showed superior olefins selectivity (C₂⁺ + C₃⁺) in the reaction of CO₂-assisted oxidative dehydrogenation of propane, keeping desired stability within 120 min. In CO₂-ODHP, the introduction of CO₂ has a significant contribution to the dehydrogenation activity of the catalysts owing to their activity on the reverse water-gas shift reaction (RWGS), although in this study the effect was less significant as very little hydrogen was produced in Ga-based catalysts, as shown in Figure S2. In this study, the
addition of CO\(_2\) significantly removed coke and thus improved the stability of the catalyst as a consequence of the coexisting Boudouard reaction.

When Na-SSZ-39(9) zeolite was used to be modified by Ga with the low SiO\(_2\)/Al\(_2\)O\(_3\) ratio, the conversion of propane is about 37% and the propane converted in the form of methane, ethylene, propylene and a small fraction of C\(_2\)H\(_6\) in Figure 2. Suppressing the side reaction, C\(_3\)H\(_6\) (~63%) and C\(_2\)H\(_4\) (~25%) constitute the other major products. A similar conclusion could be drawn for Ga-modified γ-Al\(_2\)O\(_3\), but the conversion of propane was less than 10%. The much lower activity on silica as compared to any other catalysts was explained by the lack of acid sites that catalyze the decomposition of propane.

Whether the activity promotional effect of CO\(_2\) could be observed experimentally depend largely on the coking behaviors of catalysts since the H\(_2\) lean conditions induced by CO\(_2\) result in faster deactivation of catalysts. The introduction of CO\(_2\) demonstrated an obvious promoting contribution to the dehydrogenation activity and stability of the catalysts. The conversion of CO\(_2\) on all Ga-based catalysts was low, less than 5%. However, CO\(_2\) acted as a light oxidant in the reactionary feedstock, which improved the stability of propane dehydrogenation and reduced coke formation, thus giving a stable catalytic behavior.

### 2.2. Physicochemical Properties of Modified Catalysts

The XRD patterns of the pure and Ga-modified zeolite samples are depicted in Figure 3. As shown in Figure 3, all samples displayed major diffractive indices that were identical to the bare zeolites. This signified that the zeolite’s crystalline structure of Na-ZSM-5(27), Na-SSZ-39(9) and Na-SSZ-13(28) was not affected by the loading of Ga species and the absence of any structural alteration upon metal incorporation.

![XRD spectra](image)

**Figure 3.** XRD spectra of the pure and Ga-modified zeolite samples.

N\(_2\) physisorption was used to assess the textural properties of the Ga/Na-ZSM-5(28) and Ga/Na-SSZ-39(9) catalysts. The corresponding N\(_2\) physisorption data are summarized in Table 1. As evident, the microporous surface area and microporous volume of the Ga-modified samples decreased compared to that of parent zeolite, probably due to the blocking of the pore channels by Ga\(_2\)O\(_3\) particles. This being the case, there was a slight reduction in total pore volume for the modified samples and the adsorption isotherm of type I remained (Figure S3) due to the low concentration of the Ga species.

The above topological properties indicated that between the individual samples, the topological structure of zeolites was an essential factor, but the surface area and pore volumes have a minor effect on the performance of CO\(_2\)-assisted oxidative dehydrogenation of propane.
Table 1. Textural Properties of the pure and Ga-modified zeolite samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO₂/Al₂O₃</th>
<th>(V_{\text{tot}}^a) (cm³ g⁻¹)</th>
<th>(V_{\text{micro}}^a) (cm³ g⁻¹)</th>
<th>(V_{\text{meso}}^b) (cm³ g⁻¹)</th>
<th>(S_{\text{BET}}^c) (m² g⁻¹)</th>
<th>(S_{\text{micro}}^b) (m² g⁻¹)</th>
<th>(S_{\text{meso}}^b) (m² g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-SSZ-13(27)</td>
<td>27</td>
<td>0.35</td>
<td>0.28</td>
<td>0.07</td>
<td>756</td>
<td>728</td>
<td>27</td>
</tr>
<tr>
<td>Ga/Na-SSZ-13(27)</td>
<td>27</td>
<td>0.31</td>
<td>0.24</td>
<td>0.07</td>
<td>655</td>
<td>628</td>
<td>28</td>
</tr>
<tr>
<td>Na-SSZ-39(9)</td>
<td>9</td>
<td>0.24</td>
<td>0.13</td>
<td>0.11</td>
<td>386</td>
<td>335</td>
<td>51</td>
</tr>
<tr>
<td>Ga/Na-SSZ-39(9)</td>
<td>9</td>
<td>0.24</td>
<td>0.13</td>
<td>0.11</td>
<td>382</td>
<td>326</td>
<td>56</td>
</tr>
<tr>
<td>Na-ZSM-5(27)</td>
<td>27</td>
<td>0.29</td>
<td>0.27</td>
<td>0.02</td>
<td>713</td>
<td>706</td>
<td>7</td>
</tr>
<tr>
<td>Ga/Na-ZSM-5(28)</td>
<td>28</td>
<td>0.29</td>
<td>0.26</td>
<td>0.03</td>
<td>697</td>
<td>691</td>
<td>6</td>
</tr>
</tbody>
</table>

\(^a\) Vtotal was determined from the amount of N₂ adsorbed at p/p⁰ = 0.99; \(^b\) t-plot method applied to the N₂ isotherm; \(^c\) BET method applied to the N₂ isotherm.

The acidity of catalysts was characterized by OH-FTIR, NH₃-TPD and Py-FTIR methods. The OH-FTIR spectra shown in Figure 4 suggested that the Ga/Na-ZSM-5(28) and Ga/Na-SSZ-39(9) catalysts still contained small amounts of Brønsted acid groups (3610 cm⁻¹) associated with framework aluminum (Si(OH)Al), isolated external silanol groups (3744 cm⁻¹) and non-framework aluminum groups (3662 cm⁻¹) [3]. Compared with the Ga/Na-ZSM-5(28) catalyst, the intensity of isolated external silanol groups and non-framework aluminum groups over Ga/Na-SSZ-39(9) was slightly strong, which attributed to Ga species location in zeolite channels and strong interaction with hydroxyl groups.

Figure 4. OH-FTIR spectra of the Ga/Na-ZSM-5(28) and Ga/Na-SSZ-39(9) catalysts.

Figure S4 depicted NH₃-TPD profiles with information on the acidic strength of the Ga/Na-ZSM-5(28) and Ga/Na-SSZ-39(9) catalysts, and the relative acid strength of the two samples are calculated in Table S2. In order to more clearly define the type and amount of acid sites in the samples, the NH₃-TPD plot was deconvoluted, where peaks around 230 °C were attributed to weak acids, 300 °C to moderate strong acids and 370 °C to strong acids, and the specific relative acid amounts are shown in Table S2. The Ga/Na-SSZ-39(9) catalyst contained a high concentration of medium-strong acid sites, in contrast, the Ga/Na-ZSM-5(28) sample contained a relatively high concentration of strong acid sites. To differentiate Brønsted and Lewis acid sites, pyridine adsorption and FTIR spectroscopy were conducted, as shown in Figure 5, and the Py-FTIR spectra of samples thermal treatment at 350 °C and 450 °C are shown in Figures S5 and S6, respectively. The species adsorbed at 1440 cm⁻¹ over the Ga-containing samples was assigned to pyridine molecules on Lewis acid sites. The incorporation of Ga species into the zeolite structure makes the peak at 1440 cm⁻¹ stronger compared to the pristine materials (see Figure S7). The peak at 1540 cm⁻¹ is attributed to the Brønsted acid sites, which were inherently generated by framework aluminum. When NaSSZ-39(9) zeolite was modified with Ga, the
intensity of Lewis acid sites was stronger than that of Ga/Na-ZSM-5(28) catalyst, which may be attributed to Ga species located in zeolite channels and strong interaction with bridging hydroxyl groups. However, with the increase of desorption temperature, as shown in Figures S3 and S4, the absorption peak intensity of the Ga/Na-SSZ-39(9) catalyst decreased gradually, indicating that the acidic strength of Ga/Na-SSZ-39(9) catalyst was weaker than that of Ga/Na-ZSM-5(28). This observation aligns with the NH$_3$-TPD results.

![Figure 5. Py-FTIR spectra of the Ga/Na-ZSM-5(28) and Ga/Na-SSZ-39(9) catalysts thermal treatment at 150 °C.](image)

As such, it was concluded from characterization results that except for the topological structure of the material, Lewis acid sites mainly produced by Ga ion species possessing moderate strong acidic were more favorable to CO$_2$-assisted oxidative dehydrogenation of propane. The propane dehydrogenation reaction may require the presence of Ga Lewis sites to promote heterolytic C–H bond activation.

2.3. Understanding of the Catalytic Effects Via In-Situ FT-IR Studies

According to the literature [3,44], although both Brønsted acid and Ga sites interact with propane, FT-IR results provide strong evidence suggesting that the alkyl mechanism is more likely in the CO$_2$-assisted oxidative dehydrogenation of propane on Ga-modified catalysts. Moreover, the desorption of H$_2$ is the most energy-demanding step and the existence of CO$_2$ effectively reduces the energy barriers required for the surface hydrogen removal. Therefore, in situ FTIR providing a clear picture of the dynamic surface processes involved in gas/solid heterogeneous catalysis was performed under real reaction conditions.

To compare the ability to activate propane and CO$_2$ by Ga/Na-ZSM-5(28) and Ga/Na-SSZ-39(9) catalysts, in situ FT-IR was performed to obtain the information on surface species at 600 °C and atmospheric pressure. In order to get more detailed information, the selected FT-IR profiles (3100–2750 and 2450–2200 cm$^{-1}$) are displayed in Figure 6. Over the Ga/Na-ZSM-5(28) and Ga/Na-SSZ-39(9) catalysts, the difficulty of activating propane and CO$_2$ varied depending on the topological structure of the material.

The absorbance at 2800–3000 cm$^{-1}$ was attributed to the C–H stretching vibrations. It was indicated that propane dissociative adsorption resulted in an obvious increase in surface C$_x$H$_y$ species over Ga/Na-ZSM-5(28) within 5 min which was earlier than Ga/Na-SSZ-39(9) [36]. But it was prone to activate the C–H bond of propane on Ga/Na-ZSM-5(28) catalysts, thus propane was activated before CO$_2$. The propane dehydrogenation was proposed to involve three main elementary steps: the C–H bond activation of propane on the Ga active sites, the formation of a Ga-propyl intermediate and an OH group, the subsequent β-hydride elimination, forming a hydride and propane, and the dissociation of the propene and H–H coupling to regenerate the initial Ga species [44].
The stretching vibration in the region 2400–2250 cm⁻¹, typically assigned to HCOO⁻, could be observed on co-feeding CO₂ in the reaction mixture [3]. Formic acid was proposed as an intermediate formed during the surface of catalysts. CO₂ dissociative adsorption resulted in an increase in surface HCOO⁻ species over Ga/Na-SSZ-39(9) within 5 min removing the surface hydrogen. This observation was consistent with the reaction results. Compared to Ga/Na-ZSM-5(28), due to the unique channel structure, it was more conducive to the adsorption and activation of CO₂ and the desorption of olefin intermediates, so the Ga/Na-SSZ-39(9) showed superior olefins selectivity (C₂⁺ + C₃⁺) and propylene yield in the reaction of CO₂-assisted oxidative dehydrogenation of propane, keeping desired stability within 120 min.

3. Materials and Methods

3.1. Catalysts Preparation

H-SSZ-13, H-SSZ-39 and H-ZSM-5 were purchased from Dalian Ligong Qiwangda Chemical Technology (Dalian, China). Their SiO₂/Al₂O₃ molar ratios were 27, 9 and 28, respectively (denoted as H-SSZ-13(27), H-SSZ-39(9) and H-ZSM-5(28). Na-SSZ-13(27), Na-SSZ-39(9) and Na-ZSM-5(28) zeolites were obtained by exchanging their parent zeolites four times at 353 K with 1 M solution of Sodium nitrate (NaNO₃, 99.9%), and the liquid-to-solid weight ratio was 5. The samples were filtered and washed with deionized water after each exchange, then dried at 383 K overnight. Following the final exchange, the products were calcined at 813 K for 6 h in air.
Ga/Na-SSZ-13(27), Ga/Na-SSZ-39(9), Ga/Na-ZSM-5(28), Ga/SiO2 and Ga/γ-Al₂O₃ were prepared using the incipient wet impregnation (IWI) at a liquid-to-solid weight ratio of 4. The specific modification method is as follows: firstly, calculate the required weight of gallium element according to 0.1 wt.% gallium loading, and convert it into the required weight of gallium nitrate (Ga(NO₃)₃·5H₂O, 99.9%). Then add deionized water according to 4 times the theoretical impregnation ratio, and after gallium nitrate is completely dissolved in water, slowly add zeolite powder into the solution. The mixture was then kept in a constant temperature water bath at 353 K and 300 rpm for 2 h. Finally, the mixture was centrifuged, and the solid was dried at 383 K for 12 h and calcined at 873 K in air to obtain the corresponding gallium-modified samples. The energy dispersive system (EDS) maps of aluminum, silicon and gallium of five samples are shown in Figure 7a–e, the distribution of these species is uniform, suggesting that the gallium is uniformly distributed in these carriers. Taking the case of the Ga/SSZ-39(9) catalyst, the Ga₂O₃ particles with an average size of ca. 13.8 nm are distributed on the zeolite surface, as shown in Figure 7f.

![Figure 7](image)

**Figure 7.** EDS mapping of aluminum, silicon and gallium of Ga/Na-ZSM-5 (a) Ga/Na-SSZ-39; (b) Ga/Na-SSZ-13; (c) Ga/γ-Al₂O₃; (d) Ga/SiO₂; (e) TEM image and Ga₂O₃ size distribution of Ga/SSZ-39 (f).

### 3.2. Characterization

X-ray diffraction (XRD) was recorded by a Rigaku D/Max-2004 diffractometer (Rigaku, Kyoto, Japan) with Cu Kα radiation (40 kV, 100 mA) in the 2θ range between 5 and 40°. X-ray fluorescence (XRF) measurements were conducted using a Bruker SRS3400 spectrometer (Bruker, Madison, WI, USA) to calculate the bulk silicon to aluminum ratio. Nitrogen physisorption was performed on a JWGB TB440 device at −196 °C. The samples were degassed at 350 °C for 6 h before the measurement. The surface area of all samples was determined using the Brunauer-Emmett-Teller (BET) method, with an adsorption branch in the range of P/P₀ of 0.05 to 0.30. The micro- and mesopore volumes of the samples were discriminated by the t-plot method at a P/P₀ value of 0.99. The acidity of catalysts was characterized by NH₃-TPD, OH-FTIR and Py-FTIR methods. Pyridine adsorbed FTIR spectra (Py-FTIR) were measured by a Nicolet iS50 FTIR spectrometer, and the background spectra were recorded in the region of 4000–400 cm⁻¹ with a resolution of 4 cm⁻¹ after pretreated in a vacuum at 673 K for 4 h. The catalysts were exposed to pyridine at room temperature for 0.5 h. The wafers of catalyst samples containing chemisorbed pyridine were subjected to thermal treatment at 150 °C, 300 °C and 450 °C respectively in a vacuum and cooled to room temperature, and then the IR spectra were recorded. To determine the amount of gallium in the catalyst before and after the reaction, inductively coupled plasma
optical emission spectrometry (ICP OES) was conducted on Optima 2000DV (Perkinelmer, Waltham, MA, USA). The amount of coke in the zeolites after the reaction was evaluated by thermal gravimetric analysis (TGA) on a TGA8000-Frontier-Clarus SQ8T. The sample was heated from 30 °C to 900 °C at a rate of 20 °C/min in air.

Ammonia temperature-programmed desorption (NH$_3$-TPD) characterization was conducted on a self-made instrument, using gas chromatography for real-time monitoring of exhaust gases. The samples (0.15–0.18 g, ca. 20–40 mesh) were filled in a U-reactor made in quartz and purged in helium (99.999% purity) for 1 h. Then, the temperature was cooled to room temperature for NH$_3$ adsorption, and the weakly adsorbed NH$_3$ was removed by constant helium purging. Finally, the NH$_3$-TPD profile was recorded by analyzing the exhaust gas from 150 °C to 600 °C at a rate of 15 °C/min, using helium as a carrier gas.

Fourier transform infrared spectroscopy (FT-IR) was also used to characterize the acidic properties of the prepared catalysts. The zeolite samples were pressed into thin slices (ca. 16 mg) and put in a quartz cell with CaF$_2$ windows and pretreated at 400 °C for 4 h in a vacuum (i.e., 10$^{-3}$ Pa). The samples were then naturally cooled to room temperature for subsequent measurements. The hydroxyl vibrational spectra were obtained by subtracting the background spectrum (i.e., the result measured without the sample) from the spectrum of the measured sample. The spectra for surface hydroxyl (OH) vibrations were recorded with a. The IR spectra of all samples in this paper were performed on a Nicolet iS50 FTIR spectrometer at an optical resolution of 4 cm$^{-1}$ in the range between 4000 and 400 cm$^{-1}$. In situ FTIR was performed at 300 °C and at atmospheric pressure on Ga-modified SSZ-39(9) and ZSM-5(28) catalysts for the CO$_2$-assisted oxidative dehydrogenation of propane (purity 99 wt.%, Dalian Special Gas Co., Ltd., Dalian, China) to obtain insights into the surface species on catalysts. The samples were pretreated at 400 °C under vacuum (10$^{-3}$ Pa) for 4 h. The spectra were then recorded at a resolution of 4 cm$^{-1}$ for 64 scans in the region of 4000 to 1000 cm$^{-1}$. The conversion of carbon dioxide and propane (99.9 wt.% purity) on Ga-modified Ga/Na-ZSM-5 (28) and Ga/Na-SSZ-39 (9) samples were studied using Operando Fourier transform infrared (FTIR) at 400 °C and atmospheric pressure. Several 15–20 mg samples of catalyst were pressed into self-supporting sheets (1 cm$^2$), placed in an IR cell and activated at 400 °C under vacuum (residual pressure of 10$^{-3}$ Pa) for 4 h. The spectra were recorded in the 4000–1000 cm$^{-1}$ region using a resolution of 4 cm$^{-1}$ and 64 scans.

3.3. Fixed-Bed Catalytic Tests for Propane Dehydrogenation in the Presence of CO$_2$

In this work, the performance of catalyst samples in the CO$_2$-assisted oxidative dehydrogenation of propane was tested using a continuous fixed-bed reactor. The specific testing method was as follows: the powder sample was first extruded and then ground and mashed, of which about 0.5 g of 20–40 mesh sample particles were screened and mixed with 0.5 g of inert quartz sand and loaded into a stainless-steel reaction tube with a length of 600 mm and an inner diameter of 10 mm. We used a thermocouple in contact with the center of the reaction tube to monitor the actual temperature of the reaction, and Sevenstar D08-1F&1FS Flow Readout Boxes to control the exact gas flow rate. Before the formal reaction, we purged the sample at 600° for 1 h using 60 mL/min of nitrogen to expel air and remove any adsorbed water in samples. After the pretreatment, we started to introduce the feed gas into the reaction tube to test the reaction performance of the samples, with a total inlet flow rate of 60 mL/min (C$_3$H$_8$:CO$_2$:N$_2$ volume ratio was 1:1:18). The reaction performance was evaluated by testing the reaction of each sample over 2 h at 600 °C. The product and unreacted feedstock were analyzed by inline GC 7900 gas chromatography (Techcomp, Bejing, China). This online chromatography for reaction exhaust gas detection includes two detectors, FID and TCD. The first detector is equipped with a Poraplot Q capillary column and flame ionization detector for hydrocarbon analysis, and the second detector is equipped with a Carboxen 1000 packed column (3 m × 3 mm) and thermal conductivity detector for H$_2$, CO and CO$_2$ analysis. The following equations
were used to determine the conversion of $C_3H_8$ and CO$_2$, and the selectivity of the main products ($C_3H_6$).

$$C_3H_8\text{conversion} (\%) = \frac{X_{C_3H_8(in)} - X_{C_3H_8(out)}}{X_{C_3H_8(in)}} \times 100$$

$$CO_2\text{conversion} (\%) = \frac{X_{CO_2(in)} - X_{CO_2(out)}}{X_{CO_2(in)}} \times 100$$

$$C_3H_6\text{selectivity} (\%) = \frac{X_{C_3H_6(out)}}{X_{C_3H_6(in)} - X_{C_3H_6(out)}} \times 100$$

4. Conclusions

In summary, a series of Ga-modified catalysts with different supports were successfully prepared for CO$_2$-assisted oxidative dehydrogenation of propane reaction. XRD, N$_2$-physisorption, NH$_3$-TPD, OH-FTIR and Py-FTIR characterization demonstrated that the addition of CO$_2$ effectively promoted the surface hydrogen removal, avoiding the side reaction to decrease methane and ethane over Ga/Na-SSZ-39(9) catalyst. Therefore, the Ga/Na-SSZ-39(9) catalysts showed superior olefins selectivity and catalytic stability at 600 °C compared to any other catalysts. In addition, the major difference between Ga/Na-SSZ-39(9) and Ga/Na-ZSM-5(28) lay in the C–H bond dissociation to desorb $C_3H_6$ with/without suitable adsorption ability of olefins intermediates and proper acidic strength that displayed the best catalytic performance. The reason can be ascribed to the synergistic effect of the suitable diffusion and additional active sites. This green and economically favorable synthesis route is a promising pathway for the adjustment of channel structure and acidity in zeolites for CO$_2$-assisted oxidative dehydrogenation of propane reaction.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/catal13050896/s1, FigureS1: TGA profiles for spent Ga/ZSM-5(28) after ODHP in the presence and absence of CO$_2$ under air conditions from 100 ℃ to 900 ℃. Figure S2: The performance over Ga/ZSM-5 (28) in the ODHP reaction with and without CO$_2$. Figure S3: The adsorption isotherm of the pure and Ga-modified zeolite samples. Figure S4: NH$_3$-TPD profiles of the Ga/Na-ZSM-5(28) and Ga/Na-ZSM-5(28) catalysts. Figures S5 and S6: Py-FTIR spectra of the Ga/Na-ZSM-5(28) and Ga/Na-SSZ-39(9) catalysts thermal treatment at 300 ℃ and 450 ℃ respectively. Figure S7: Py-FTIR spectra of the Ga/ZSM-5 (28), Ga/Na-SSZ-39(9) samples and their pristine materials. Table S1. ICP-OES measurements of the Ga-based catalysts before and after the reaction. Table S2. Relative acid strength of Ga/Na-ZSM-5(28) and Ga/Na-SSZ-39(9) catalysts.

Author Contributions: W.Z. supervised the work; W.Z. conceptualized and designed the experiments, analyzed the results, and wrote the manuscript; Y.J. wrote the manuscript and performed the catalyst preparation, characterization and catalytic tests; Z.S., S.Z., E.X., Y.H., G.C. and Y.Z. performed characterization and catalytic tests. All authors have read and agreed to the published version of the manuscript.

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