

Review

Recent Progress of Ga-Based Catalysts for Catalytic Conversion of Light Alkanes

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Abstract: The efficient and clean conversion of light alkanes is a research hotspot in the petrochemical industry, and the development of effective and eco-friendly non-noble metal-based catalysts is a key factor in this field. Among them, gallium is a metal component with good catalytic performance, which has been extensively used for light alkanes conversion. Herein, we critically summarize recent developments in the preparation of gallium-based catalysts and their applications in the catalytic conversion of light alkanes. First, we briefly describe the different routes of light alkane conversion. Following that, the remarkable preparation methods for gallium-based catalysts are discussed, with their state-of-the-art application in light alkane conversion. It should be noticed that the directional preparation of specific Ga species, strengthening metal-support interactions to anchor Ga species, and the application of new kinds of methods for Ga-based catalysts preparation are at the leading edge. Finally, the review provides some current limitations and future perspectives for the development of gallium-based catalysts. Recently, different kinds of Ga species were reported to be active in alkane conversion, and how to separate them with advanced in situ and ex situ characterizations is still a problem that needs to be solved. We believe that this review can provide base information for the preparation and application of Ga-based catalysts in the current stage. With these summarizations, this review can inspire new research directions of gallium-based catalysts in the catalysis conversion of light alkanes with ameliorated performances.

Keywords: light alkane; gallium; catalysis; olefins



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1. Introduction

Light olefins, mainly ethylene, propylene, and butenes, are the basic organic materials for the production of many downstream high-value-added products, such as polyvinyl chloride, polypropylene, etc., as shown in Figure 1 [1,2]. Steam cracking and fluid catalytic cracking are the main sources of light olefins production at present. A lot of countries announced to achieve carbon neutrality in the next 40 years, and this makes the clean and efficient production of light olefins become one of the most important directions in the current chemical industry. Until 2021, the global demand for ethylene and propylene reached more than 200 and 100 million tons, respectively. The efficient and clean conversion of light alkanes to produce light olefins, including alkane dehydrogenation, aromatization, cracking, etc., is more energy-saving than traditional processes. Therefore, how to reasonably and efficiently utilize abundant alkane resources has become a research hotspot in the field.

1.1. Overview of Catalytic Conversion Routes of Light Alkanes

There are many light alkanes catalytic conversion routes, such as dehydrogenation, aromatization, catalytic cracking, and isomerization, and different kinds of downstream products can be produced, as shown in Figure 2.

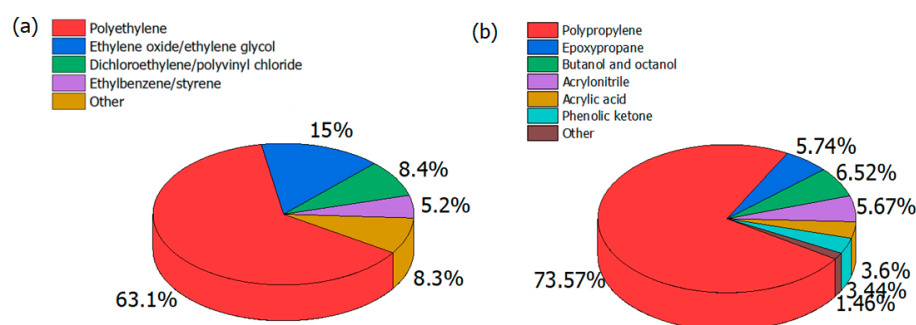


Figure 1. Downstream product consumption of ethylene (a) and propylene (b) [1,2].

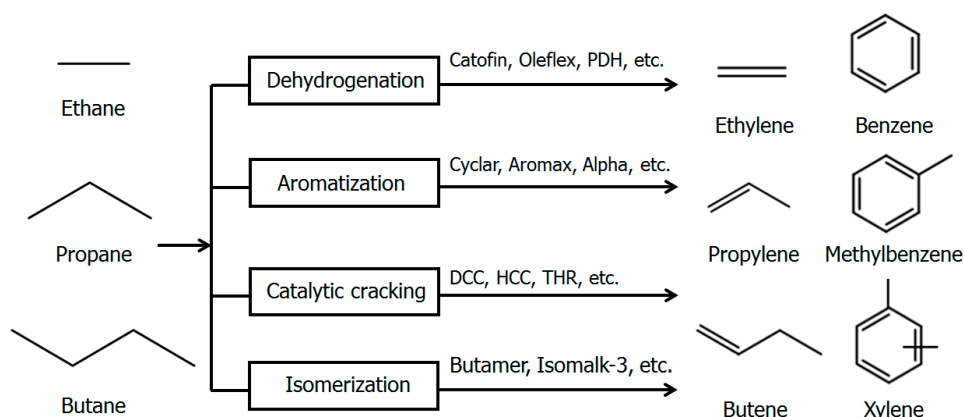


Figure 2. Schematic diagram of downstream products from catalytic conversion of light alkanes and their industrial processes.

1.1.1. Dehydrogenation

Light alkane dehydrogenation aims to directionally convert light alkanes into light alkenes, such as ethylene, propylene, etc., at a temperature ranging from 500 to 680 °C. Compared with steam cracking and catalytic fluid cracking, it can greatly improve the yield of light alkenes because of the single raw material and easy separation of products. Albeit, with the limitation of thermodynamics, the equilibrium conversion of alkane dehydrogenation is relatively low. Moreover, the commercialized catalysts, including Pt- and Cr-based ones are costly.

At present, the main commercialized propane dehydrogenation processes include Catofin, Oleflex, Linde, PDH, FBD-4, STAR, etc. Light alkanes possess high C-H bond activation energy, and the equilibrium conversion is thermodynamically limited. This makes efficient alkane dehydrogenation challenging and attractive. The non-oxidative alkane dehydrogenation is an endothermic process, and it requires high temperature and/or low partial pressure reaction conditions to obtain a high olefin yield. Moreover, the activation of olefins is much easier than alkanes. And a high reaction temperature or high reactant concentration will lead to thermal cracking and the formation of coke, thereby decreasing catalytic efficiency. Therefore, it is of great significance to develop catalysts with high selectivity, activity, and coke resistance ability.

The abundant active components, such as Pt-Sn [1–6], CrO_x [7–13], VO_x [14–21], GaO_x [22–25], and nano-carbon [26–29], are an important active species for alkane dehydrogenation. Pt-Sn catalyst has been used in UOP industrial process, and the CrO_x-Al₂O₃-based catalyst has been industrialized in the Catofin process. However, at present, the high cost of platinum-based catalysts and the environmental harm of CrO_x-based catalysts, especially Cr⁶⁺ species, cannot be ignored. Thus, the development of inexpensive and eco-friendly non-noble metal-based dehydrogenation catalysts attract much attention.

1.1.2. Aromatization

BTX (including benzene, toluene, and xylene) are important raw materials for the synthesis of polystyrene, nylon, resin, etc. At present, the petroleum refining process is the main source for aromatic hydrocarbons production. With the decrease in oil reserves and the development of shale gas exploration technology, it is more attractive to use light alkane aromatization to promote aromatics production. Besides BTX, light alkane aromatization can produce ethylene and propylene at the same time. While, at present, light alkane aromatization still suffers from low aromatics selectivity and the deactivation of catalysts. Cyclar, Aromax, Alpha, and Zeoforming are the main commercialized aromatization processes. However, the aromatization reaction of alkanes usually requires a high temperature to achieve high alkanes conversion and aromatics yield, leading to high coke deposition.

ZSM-5 is a zeolite with MFI topology, with 10-membered ring straight channels (5.1×5.5 Å) and unique zigzag straight channels (5.3×5.6 Å). It has good shape-selective catalytic performance in the aromatization of light alkanes. However, there are some problems such as low aromatic selectivity and high coke deposition to make it possess low stability. By the introduction of aromatized metal components, such as Ga [30–35], Ni [36], Cr [37], Zn [38,39], Mo [40], etc., to construct bifunctional catalysts, these problems can be effectively solved.

1.1.3. Catalytic Cracking

During the decades, the development of catalytic cracking with energy-saving and efficiency-enhancing properties is an important direction for ethylene and propylene production. Compared with steam cracking, it can decrease the reaction temperature and the yield of CO₂, with higher selectivity to the main products. Additionally, it also has the advantages of adjustable product distribution, a high yield of the target product, and low energy consumption. Up to now, the light alkane-based catalytic cracking still needs to promote its yield of propylene and ethylene. Therefore, it should focus on the development of catalytic cracking catalysts in the future. Moreover, improving the anti-coking ability and increasing the stability are still critical in this field.

Some commercialized processes for catalytic cracking are reported, such as DCC and CPP processes from the China petrochemical research institute, the THR process from the Toyo engineering corporation. Similar to the alkane aromatization, ZSM-5 zeolite is an important catalyst for the catalytic cracking. To improve the catalytic performance further, the development of non-noble metal bifunctional catalysts is particularly important for catalytic cracking. With the introduction of metal components, which can dehydrogenate light alkane into olefins first, the conversion of alkane can be improved to a large extent. Pt [41,42], Ga [43], Zn [44,45], Fe [46,47], etc., have been reported to efficiently build bifunctional catalysts with HZSM-5 as a catalytic cracking active component.

1.1.4. Isomerization

The octane number of n-alkanes is much lower than that of isomerized alkanes. Therefore, light alkane isomerization is mainly used to produce high value-added oil-based products such as high-grade lubricating oil and high-quality fuel oil, which is of great significance to modern petrochemical and refining industries. The isomerization of alkanes is an effective route to improve the octane number of straight-run gasoline and the performance of diesel and engine oil at a low-temperature [48]. The produced isomerization oil possesses a high octane number and does not have sulfur, olefins, or aromatics. The UOP Butamer low temperature isomerization process, BP low temperature isomerization process, GTC Isomalk-3 low temperature isomerization process, etc., are reported to be successful commercialized processes. At present, except for increasing product yield, the coke deposition and loss of active species urgently need to be solved.

The common catalysts for isomerization are chlorinated alumina-supported platinum-based catalysts [49] and zeolite-supported platinum [50–52] or palladium-based [53] catalysts. The former can be operated at a low temperature (<180 °C) and produce high octane

branched alkanes. However, the catalyst is sensitive to water and impurity, and chlorine treatment is needed in the operation process to avoid the loss of activity, resulting in certain environmental problems. For zeolite-supported platinum or palladium-based catalysts, higher operating temperatures ($\sim 250\text{ }^{\circ}\text{C}$) are needed, and thermodynamic constraints lead to the lower yield of branched isomers. Therefore, it is necessary to develop environmentally friendly catalysts for the isomerization of light alkanes at a low temperature.

A solid acid catalyst composed of non-noble metal oxides is one of the most promising new catalysts at present, such as a WO_3/ZrO_2 catalyst, which shows good activity for the isomerization of light n-alkanes at a moderate temperature. Additives, including Fe [54], Al [54,55], Ga [55], and Zn [56], can improve the activity of WO_3/ZrO_2 . Among them, Ga is one of the most effective additives [57].

1.2. Importance of Ga-Based Catalysts

In recent years, non-noble metal active species such as Ni [58], Zn [59], Ga [60], Mo [61], Co [62], and Fe [63] have shown unique advantages in the field of light alkanes conversion. The Ga component has demanded much attention over the decades. For example, a Zn-Ga-modified ZSM-5 catalyst was reported to exhibit excellent light aromatics production in a methane environment due to its synergistic effect on the aromatization of long-chain alkanes [64]. Based on characterization analysis, the authors concluded that highly dispersed Zn and Ga species increased the amount of Lewis acid sites, which can effectively promote methane conversion on a Zn-Ga/ZSM-5 catalyst. It is believed that non-noble metal-based catalysts, including Ga species, would be promising in the future as potential candidates in light alkane conversion to replace noble metals and other environmentally hazardous components.

The fraction of gallium in the earth accounts for about 0.015%, which is dispersed widely. However, more than 99% of gallium is associated with zinc, aluminum, and germanium minerals, which is a kind of associated ore. Usually, gallium is mainly extracted from the zinc and aluminum smelting process. Global gallium production reached 300 tons in 2020. In the catalysis field, gallium species have the advantages of good hydrothermal stability, high catalytic activity, non-toxicity, and eco-friendliness [65]. Therefore, it receives extensive attention and wide uses in multifunctional materials, coal-to-olefins, petroleum cracking, and other related fields.

Ga_2O_3 is a metal oxide with good catalytic performance in alkane conversion, which has attracted great interest. Such as in the study of Rochlitz et al. [66], Ga_2O_3 -based catalysts can be used to convert propane to aromatics through dehydrogenation. However, Ga_2O_3 is easily reduced during the reaction process, and the catalyst may undergo rapid deactivation, which makes it difficult to be used in industrial-scale utilization. Further detailed investigation on Ga-based catalysts in alkane conversion is ongoing.

2. Basic Properties and Preparation Methods of Ga-Based Catalysts

2.1. Basic Information about Ga Species

Ga belongs to the IIIA group, and the configuration of its outer electron layer is $3d^{10}4s^24p^1$. The valence of Ga is usually +2 or +3, and its chemical compounds with +3 valence are usually the most stable ones. As a typical rare-dispersed metal, some of its properties are close to amphoteric metals. Due to this, Ga is a relatively safe metal species, which can be dissolved in an acid and alkali solution and is harmless to the environment.

Various Ga species are deemed as active species in catalytic reactions, including gallium-based alloys, gallium-based oxides, gallium-based hydroxides, and other types. Ga-based alloys contain Ga components with the addition of other metals, such as W, Co, Ti, Fe, and so on. At present, in zeolite-supported Ga-based catalysts, the effect of Ga species properties on catalytic performance has been extensively investigated [67]. Taking the form of Ga species in +3 valence as an example, the possible active species are deemed to be $[\text{GaO}]^+$, $[\text{Ga}_2\text{O}_2]^+$, $[\text{Ga}(\text{OH})]^{2+}$, $[\text{Ga}(\text{OH})_2]^+$, $[\text{GaH}_2]^+$, $[\text{GaH}]^{2+}$, Ga^+ and/or GaO_x clusters [68–74]. A variety of oxygenated gallium species, such as monomer $[\text{GaO}]^+$ or

dimer $[\text{Ga}_2\text{O}_2]^{2+}$ are also reported [68]. In addition, according to the different pretreatment conditions, different types of Ga species, such as gallium oxide aggregates and reduced gallium ion species, can be formed.

2.2. Preparation Method of Ga Catalyst

At present, the common preparation methods of gallium-based catalysts mainly include the impregnation method, ion-exchange method, chemical liquid deposition method, and in situ synthesis method. A summary of Ga-based catalysts mentioned in this work is listed in Table 1.

Table 1. Summary of presentative Ga-based catalysts with different preparation methods.

No.	Support	Ga Precursor	Preparation Method	Application	Active Species	Ref.
1	NaZSM-5	$\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$	Impregnation	Ethane dehydrogenation	Ga_2O_3	[22]
2	SiO_2	$\gamma\text{-Ga}_2\text{O}_3$	Impregnation	Propane dehydrogenation	$\text{Ga}^{3+}_{\text{IV}}$ sites	[60]
3	ZSM-5	$\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$	Impregnation	Propane dehydrogenation	Ga_2O_3	[24]
4	$\gamma\text{-Al}_2\text{O}_3$	$\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$	Impregnation	Propane dehydrogenation	$\text{Ga}^{\delta+}\text{-H}$	[25]
5	HZSM-5	$\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$	Impregnation	Catalytic hydrocracking		[31]
6	HZSM-5	$\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$	Impregnation	Propane aromatization	Bulky Ga agglomerates, dispersed Ga_2O_3 and GaO^+ ion	[32]
7	HZSM-5	$\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$	Impregnation	Methanol to aromatic	Ga_2O_3	[33]
8	HZSM-5	$\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$	Impregnation	Ethylene aromatization	Ga_2O_3	[34]
9	HZSM-5	$\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$	Impregnation	Propane aromatization		[37]
10	HZSM-5	$\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$	Impregnation	Ethane aromatization	Ga^+	[40]
11	ZrO_2	$\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$	Impregnation	Butane isomerization		[55]
12	ZrO_2	$\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$	Impregnation	Hexane isomerization	Ga^{3+}	[57]
13	HZSM-5	$\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$	Impregnation	Light alkanes aromatization		[64]
14	HZSM-5	$\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$	Impregnation	Ethane aromatization	GaO^+	[70]
15	ZSM-5/SBA-15	$\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$	Impregnation	Catalytic pyrolysis		[75]
16	SiO_2	$\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$	Impregnation	CO_2 to methanol	NiGa alloy	[76]
17	HZSM-5	$\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$	Impregnation	Propane dehydroaromatization		[77]
18	ZSM-5	$\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$	Impregnation	Propane dehydroaromatization	$\text{Ga}^{\delta+}$ cations, $\delta < 2$	[78]
19	SiO_2	$\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$	Impregnation	Propane dehydroaromatization	Four-coordinate $\text{Ga}^{3+}\text{-O}$ centers	[79]
20	HZSM-5	$\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$	Impregnation	Propane aromatization	$\text{Ga}^+/\text{GaH}_2^+$ pair	[80]
21	HZSM-5	$\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$	Impregnation	Propane aromatization	GaO^+	[81]
22	HZSM-5	trimethylgallium	Chemical vapor deposition	Propane dehydrogenation	$[\text{GaH}_2]^+$, GaO^+ , Ga^+	[71]
23	HZSM-5	trimethylgallium	Chemical vapor deposition	Propane dehydrogenation	Dimeric oxygen-bridged Ga species	[72]
24	HZSM-5	$\text{GaCl}_3 \cdot 6\text{H}_2\text{O}$	Chemical vapor deposition	Propane dehydrogenation	$[\text{GaH}_2]^+$	[82]
25	HZSM-5	$\text{GaCl}_3 \cdot 6\text{H}_2\text{O}$	In situ synthesize	Methanol to aromatic		[35]
26	HZSM-5	$\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$	In situ synthesize	Propane dehydrogenation	Framework Ga_{FW}	[82]
27	HZSM-5	$\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$	Ion-exchange	Pentane aromatization	$[\text{GaH}_2]^{2+}$	[30]
28	HZSM-5	$\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$	Ion-exchange	Benzene alkylation	Non-framework $\text{Si-O}(\text{Ga}^{x+})\text{-Al}$	[43]
29	HZSM-5	$\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$	Ion-exchange	Pentane aromatization	$[\text{GaH}_2]^+$	[67]
30	HZSM-5	$\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$	Ion-exchange	Propane dehydrogenation	$[\text{GaH}_2]^+$	[82]
31	SiO_2	$\text{Ga}(\text{OSi}(\text{OtBu})_3)_3(\text{THF})$	Surface organometallic chemistry	Propane dehydrogenation	Ga(III) isolated sites	[66]
32	H-MFI	$\text{GaCl}_3 \cdot 6\text{H}_2\text{O}$	Vapor phase exchange	Propane dehydrogenation and Cracking	$[\text{GaH}_2]^+$	[68]
33	H-MFI	$\text{GaCl}_3 \cdot 6\text{H}_2\text{O}$	Vapor phase exchange		$[\text{GaH}_2]^+$, $[\text{Ga}(\text{OH})_2]_2^+$, $[\text{Ga}(\text{OH})_2]^{2+}\text{-H}^+$ cation pairs, $[\text{Ga}(\text{OH})\text{H}]^+\text{-H}^+$ cation pairs, etc.	[83]

2.2.1. Impregnation

The impregnation method is to place the support in the solution, which contains the precursors of active components, and realizes the introduction of metal species through the diffusion process of the precursor solution. When the above process reaches equilibrium, the as-desired sample can be then obtained by drying, calcination, and activation.

Impregnation is a general method for preparing various metal species with an as-designed metal content. Its advantage lies in the wide range of applications and can choose any needed support. It is widely used in the preparation of supported catalysts, especially for noble metal catalysts with low content. However, it is conquered at a high metal loading introduction, which leads to the inhomogeneous dispersion of the active component and metal sintering. This finally affects the catalytic activity.

Ga species obtained by impregnation tend to exist in the form of gallium oxide aggregated on the outside surface of the support. Yang et al. [75] successfully prepared a Ga/ZSM-5/SBA-15 composite catalyst by the impregnation method. SEM-EDS, XRD, and Py-FT-IR analysis showed that Ga was uniformly dispersed on the surface of ZSM-5/SBA-15, and the agglomeration was not obvious. With the increase of the Ga content, the density of Brønsted acid sites decreased and Lewis acid sites increased. The as-prepared Ga-based catalyst had higher BTX selectivity in the catalytic decomposition of rice husk, and the BTX yield increased from 18.0% to 25.5%.

Nguyen's research group [76] prepared a Ni-Ga/mesoporous SiO₂ catalyst by the impregnation method and investigated their catalytic performance in the synthesis of methanol from CO₂. The as-prepared Ni-Ga bimetallic catalyst mainly contains a crystalline δ -Ni₅Ga₃ phase, which is uniformly dispersed on the support. The as-formed δ -Ni₅Ga₃ species can greatly improve the CO₂ reduction conversion and target product selectivity, showing a good application prospect.

2.2.2. Ion Exchange

The ion-exchange method uses the precursor salt of active components that can be exchanged on the surface of the support to anchor the active components, and the supported metal catalyst can be then prepared after washing, drying, and activation. The ion-exchange method can make the high dispersion and uniform distribution of active components, which is especially suitable for the preparation of noble metal-based catalysts with low content. It is also a common method for heterogeneous catalysts and zeolite modification.

By modulating the physical and chemical properties of the support, such as the Si/Al ratio of zeolite in the catalyst, the ion exchange degree can be adjusted. A gallium cation was loaded on HZSM-5 zeolite by ion-exchanging zeolite with a gallium nitrate solution by Wannapakdee et al. [67]. The synergistic matching between the Ga species and HZSM-5 can be adjusted by controlling the Si/Al ratio of HZSM-5 zeolite and the precursor Ga(NO₃)₃ solution at 353 K. Except for ion exchange, different preparation methods including in situ synthesis and impregnation were also introduced [67]. With the combination of EXAFS, ⁷¹Ga NMR, and H₂-TPR, the impregnated- and in situ-synthesized samples were found to possess the octahedral-coordinated bulk Ga₂O₃ particles. For the ion-exchanged one, well-dispersed Ga species and/or small Ga, mainly GaH²⁺, would exist on ZSM-5. The as-prepared Ga/HZSM-5 catalysts were used for the aromatization of n-pentane. The author confirmed that different Ga species exhibited different catalytic performances, and it was found that the ion-exchanged sample, with more GaH²⁺ formation, has the highest n-pentane conversion and BTX (benzene, toluene, and xylene) selectivity of more than 50% and 40%, respectively. This work indicates that the preparation method can modulate the formation of different kinds of Ga species, which will change the catalytic performance.

A series of Ga-ZSM-5 catalysts were prepared by Zhou et al. [82] with an ion-exchange method through stirring the commercial ZSM-5 and Ga(NO₃)₃ solutions for 24 h. The samples were dried overnight after the ion-exchange process and calcined to obtain the final product. XAS and NMR analysis revealed that this preparation method can form Ga-Lewis site and framework Ga species (Ga_{FW}) with high activity in zeolite, and the as-prepared catalyst possesses good aromatization activity in the formation of aromatic hydrocarbons. Total BTX selectivity is up to 57%, nearly four times higher than that of commercial HZSM-5.

Ga/H-MFI catalysts with Ga/Al ratios in the range of 0.1–0.7, prepared by a gas-phase ion-exchange method with H-MFI and GaCl_3 , were reported by Bell's group [83]. In this process, the -OH group on the H-MFI zeolite forming Brønsted acid sites can be exchanged by a monovalent $[\text{GaCl}_2]^+$ cation. A high Ga cation exchange degree can be achieved. To completely remove the Cl-containing ligand of the grafted Ga species, $[\text{GaCl}_3]^+/\text{H-MFI}$ samples were treated at a high temperature under a hydrogen atmosphere, and more than 95% of the Cl element can be removed.

Their further study found that when $\text{Ga}/\text{Al} = 0.1$, about 50% of $[\text{GaH}_2]^+$ cations would be oxidized to divalent $[\text{Ga}(\text{OH})]^{2+}$ cations. The pair Al species with an Al–Al distance greater than 5 Å can bind to the divalent $[\text{Ga}(\text{OH})]^{2+}$ cations. The remaining $[\text{GaH}_2]^+$ cations are oxidized to $[\text{Ga}(\text{OH})_2]^+-\text{H}^+$ species. If the Ga/Al ratio is greater than 0.1, Ga^{3+} appears in the form of a $[\text{Ga}(\text{OH})_2]^+-\text{H}^+$ cation pair. Neutral GaO_x species were formed when the Ga/Al ratio was greater than 0.3, independent of the H-MFI framework. Figure 3 summarizes the variation of Ga^{3+} species with the Ga/Al ratio in oxidized and reduced Ga/H-MFI. This study provides important information for understanding the variation of Ga^{3+} species in the dehydrogenation and cyclization of light alkanes.

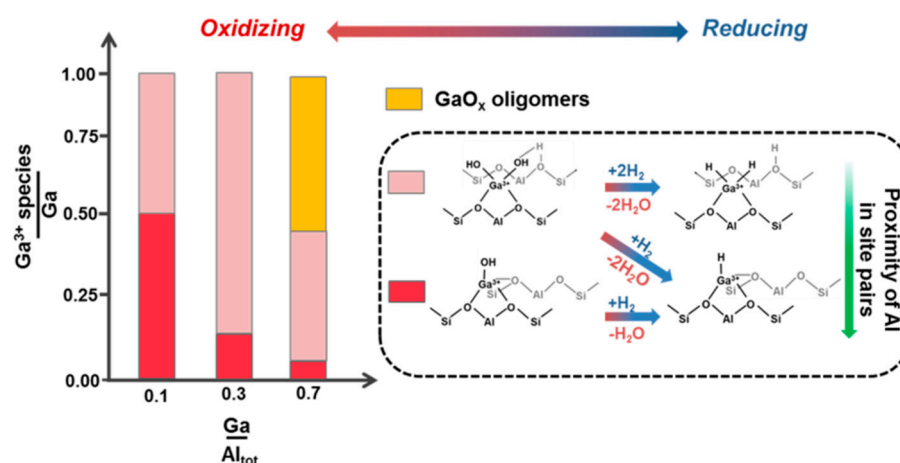


Figure 3. Ga^{3+} species in Ga/H-MFI under oxidizing (red) and reducing conditions (blue). Reprinted with permission from ref. [83]. Copyright 2018 American Chemical Society.

2.2.3. Chemical Liquid Deposition

A simple and low-cost chemical liquid deposition (CLD) method using non-toxic liquid precursors was developed by Sun et al. [84]. The equipment is simple, inexpensive, and easy to operate, and the as-grown films are dense and uniform. This CLD method can be used for the efficient introduction of catalytic active components and the surface modification of the catalysts. The introduced metal species can be interacted with the hydroxyl groups of the zeolite, and after high-temperature calcination, the as-formed oxide coating can be deposited on the surface of the zeolite. This oxide coating can passivate the acid center of the outside zeolite and reduce the pore size. This method exhibits broad application prospects in the field of shape-selective catalysis, including Ga-based catalyst modification.

Xu et al. [77] prepared a series of silylated Ga/ZSM-5 catalysts by chemical liquid deposition method and evaluated their catalytic performance in propane aromatization. Ga/ZSM-5 was firstly prepared by the impregnation method with $\text{Ga}(\text{NO}_3)_3$ as the precursor. Then, the target SiO_2 -coated Ga/ZSM-5 catalyst was obtained with n-hexane as a solvent and tetraethoxysilane as a modifier. By modulating the CLD time, the Si/Ga ratio was adjusted, and the pore size of the catalyst was reduced, which significantly improved the selectivity to p-xylene. Through the characterization analysis, it was found that the introduction of SiO_2 on the outside surface of the catalyst prepared by the CLD method was beneficial to passivate the external strong acid center, and, finally, inhibited the side reaction

of propane cracking. BTX selectivity can reach 55% at 49% of propane conversion over the as-prepared Ga sample by CLD, which were all higher than those of the conventional impregnation Ga/HZSM-5 sample.

2.2.4. In Situ Synthesis

The in situ synthesis method mainly uses a Ga precursor and zeolite precursor to directly synthesize catalysts through the one-pot preparation processes such as co-precipitation, hydrothermal crystallization, or a one-step direct synthesis. The dispersion of Ga species can reach a high level, with enhanced metal-support interaction, resulting in the improvement of catalytic performance.

Zhou et al. [82] used the in situ synthesis method to prepare a series of Ga-ZSM-5 catalysts and applied them in ethylene dehydroaromatization. After mixing a certain amount of TEOS, sodium aluminate, and gallium nitrate under alkaline conditions, the as-mixed sol was treated under the hydrothermal condition at 170 °C. The co-crystallization of the mixture containing Ga species, silicon components, and aluminum components can be then achieved, and Ga-ZSM-5 catalysts can be directly synthesized. Meanwhile, for comparison, the samples were also prepared by the ion-exchange method and chemical vapor exchange method. It was found that over the samples prepared by in situ synthesis, the framework Ga species, as Lewis acid sites and extra-framework Ga_{EFW} species, participate in the reaction together, and the formed Ga(framework)-Ga(extra-framework) pair was the most favorable to form aromatic molecules, thus, promoting the efficient synthesis of aromatic products.

3. Application of Ga-Based Catalysts in Light Alkane Conversion

With the above-mentioned, Ga-based catalysts have caught much attention in light alkane conversion, and the summary of their catalytic performance is listed in Table 2. A detailed discussion of their application is shown in the following section.

Table 2. Summary of the application of Ga-based catalysts on alkane conversion.

Catalyst	Preparation Method	Application	Alkane Concentration	Temp. (°C)	Conv. (%)	Product Select. (%)	Reactant	Products	Ref.
Ga/ZSM-5-N	Impregnation	Dehydrogenation	$C_2H_6/CO_2/N_2 = 3/15/82$	650	3.3	90.9	C_2H_6	C_2H_4	[22]
Ga/ZSM-5-S	Impregnation				25.3	91.7			
Ga/ZSM-5-L	Impregnation				2.2	97.5			
Ga/ZSM-5-S	Impregnation				24.9	84.2			
0.03Pt-3Ga ₂ O ₃	Impregnation	Dehydrogenation	$C_3H_8/H_2/N_2 = 14/14/72$	600	12	95	C_3H_8	C_3H_6	[25]
TMG/ZSM-5	Chemical vapor deposition	Dehydrogenation	$C_3H_8/He = 1/19$	550	24	63	C_3H_8	C_3H_6	[71]
Ga/ZSM-5	Chemical vapor deposition	Dehydrogenation	$C_3H_8/He = 1/19$	550	7	80	C_3H_8	C_3H_6	[72]
Ga ₂ O ₃ /MCM-22	Impregnation	Dehydrogenation	$C_3H_8/Ar = 1/19$	600	57.8	37.5	C_3H_8	C_3H_6	[78]
Ga ₂ O ₃ /ITQ-2	Impregnation				30	72			
Ga ₂ O ₃ /HZSM-48	Impregnation				40	53.8			
Ga ₂ O ₃ /TiO ₂	Impregnation				23	85			
Ga ₂ O ₃ /Al ₂ O ₃	Impregnation				33	92			
Ga ₂ O ₃ /ZrO ₂	Impregnation				39	74			
Ga ₂ O ₃ /SiO ₂	Impregnation				7.2	92			
Ga ₂ O ₃ /MgO	Impregnation				5.3	34			
Ga ₂ O ₃ /Al ₂ O ₃	Impregnation				46	95.2			
Ga ₂ O ₃ /ZSM-5	Impregnation				78.1	60.2			
Ga ₂ O ₃ /SiO ₂	Impregnation				6.7	90.1			
Ga ₂ O ₃ /SBA-15	Impregnation				28.5	92.5			
γ-Ga ₂ O ₃	Alcoholic coprecipitation				41.3	93.3			
Ga ₈ Al ₂ O ₁₅	Alcoholic coprecipitation				51.7	91.6			
Ga ₅ Al ₅ O ₁₅	Alcoholic coprecipitation				38.4	92.3			
Ga ₂ Al ₈ O ₁₅	Alcoholic coprecipitation				22.8	94.9			

Table 2. Cont.

Catalyst	Preparation Method	Application	Alkane Concentration	Temp. (°C)	Conv. (%)	Product Select. (%)	Reactant	Products	Ref.
1000 ppm Pt, 1.5 wt% Ga, 0.25 wt% K	Impregnation				42	96.7			
1000 ppm Pt, 3 wt% Ga, 0.25 wt% K	Impregnation				41.9	96.9			
1000 ppm Pt, 1.5 wt% Ga	Impregnation	Dehydrogenation	Pure C ₃ H ₈	620	42	96.7	C ₃ H ₈	C ₃ H ₆	[86]
1000 ppm Pt, 3 wt% Ga	Impregnation				40.3	95.4			
1.5 wt% Ga, 0.25 wt% K	Impregnation				14.7	88.9			
3 wt% Ga, 0.25 wt% K	Impregnation				21.8	89			
1.5 wt% Ga	Impregnation				15.8	81.3			
3 wt% Ga	Impregnation				20.7	88			
Ga/Z-0.2HA	Impregnation	Aromatization	C ₃ H ₈ /N ₂ = 1/2	550	82.5	53.3	C ₃ H ₈	BTX	[32]
2Ga/Z	Impregnation				82	48.8			
2% Ga/ZSM-5	Impregnation			450	99.7	53.4			
2% Ga/ZSM-5	Impregnation			550	99.2	63.6			
2% Ga/ZSM-5	Impregnation	Aromatization	C ₂ H ₄ /H ₂ /N ₂ = 1/1/1	630	98.7	54.2	C ₂ H ₄	BTX	[34]
2% Ga/ZSM-5 ST-1	Impregnation			450	99.2	46.6			
2% Ga/ZSM-5 ST-1	Impregnation			550	98	67.9			
2% Ga/ZSM-5 ST-1	Impregnation			630	97.5	65.9			
2Cr-Ga/Z5	Impregnation	Aromatization	C ₃ H ₈ /N ₂ = 1/2	540	51	55	C ₃ H ₈	BTX	[37]
Ga/ZSM-5	Impregnation		Pure C ₂ H ₆	650	17.5	67	C ₂ H ₆	C ₂ H ₄	
Ga/ZSM-5	Impregnation	Aromatization	Pure C ₂ H ₆	650	17.5	21	C ₂ H ₆	BTX	[40]
GaExcZS-5-NS-38	Ion-exchange	Aromatization	C ₅ H ₁₂ /N ₂ = 1/9	500	86	43.25	C ₅ H ₁₂	BTX	[67]
5% Zn-Ga/ZSM-5	Impregnation	Aromatization	Heptane with methane	400	98.16	58.56	Heptane	BTX	[64]
1% Ga/ZSM-5	Impregnation		Heptane with methane		97.71	37.45	Heptane	BTX	
H-Ga-ZSM-5	Chemical vapor deposition	Aromatization	C ₂ H ₄ /Ar = 1/7	400	94	52	C ₂ H ₆	BTX	[82]
Ga/Z5-4Si	Impregnation	Aromatization	C ₃ H ₈ /N ₂ = 1/2	540	40.29	53.47	C ₃ H ₈	BTX	[77]
Ga/IMRO3C	Impregnation	Aromatization	C ₃ H ₈ /N ₂ = 1/2	540	61	60	C ₃ H ₈	BTX	[81]
H-Ga/SNSA	impregnation and in situ treatment	Aromatization	C ₃ H ₈ /N ₂ = 1/2	540	53.6	58	C ₃ H ₈	BTX	[87]
Pt/1.0GWZ850	Impregnation	Isomerization	C ₄ H ₁₀ /H ₂ /Ar = 3/12/120	300	44	91	n-C ₄ H ₁₀	i-C ₄ H ₁₀	[55]
1.0% Re/1.0% Ga ₂ O ₃ /WO ₃ /ZrO ₂	Impregnation	Isomerization	C ₆ H ₁₄ /N ₂ = 1/2	195	84.8	97.7	n-C ₆ H ₁₄	i-C ₆ H ₁₄	[57]
SZG/MCM-41	Impregnation	Isomerization	n-C ₄ H ₁₀ /H ₂ = 1/10	250	43.85	87.5	n-C ₄ H ₁₀	i-C ₄ H ₁₀	[88]
Pt/H-ZG-1	Impregnation	Isomerization	n-dodecane/H ₂ = 1/100	320	90	78.2	n-C ₁₂ H ₂₆	i-C ₁₂ H ₂₆	[89]
0.1% Ga ₂ O ₃ /ZSM-5	Impregnation				47.3	84.5			
0.2% Ga ₂ O ₃ /ZSM-5	Impregnation				82.3	84.7			
0.3% Ga ₂ O ₃ /ZSM-5	Impregnation	Catalytic cracking	n-C ₄ H ₁₀ /N ₂ = 1/19	600	93.8	79.2	n-C ₄ H ₁₀	Alkene + BTX	[90]
0.4% Ga ₂ O ₃ /ZSM-5	Impregnation				96.5	82.1			
0.3% Ga ₂ O ₃ /ZSM-5 Fibers	Impregnation				99.9	87.7			
Redox-Ga/ZSM-5-0.7	Impregnation	Catalytic cracking	n-C ₄ H ₁₀ /N ₂ = 1/19	600	99	80	n-C ₄ H ₁₀	Alkene + BTX	[91]

3.1. Ga-Based Catalysts in Alkane Dehydrogenation

As mentioned above, the dehydrogenation of light alkanes is one of the most significant routes for the directional production of light olefins, and the development of non-noble metal-based catalysts is an important research direction at present. Compared with the traditional Cr-based and Pt-based catalysts, Ga-based catalysts have become an excellent candidate due to their unique ability to activate hydrocarbon species. Nakagawa et al. [78] found that β -Ga₂O₃ exhibited the highest ethane dehydrogenation activity in all polycrystalline forms due to its abundant surface. The typical sample showed 32.0% and 90.0% for initial ethane conversion and propylene selectivity, respectively. Additionally, the final ethane conversion reached 17.0% after a 30 h time-on-stream reaction. Using density functional theory, Abdelgaid et al. [92] studied the non-oxidative dehydrogenation reactions of ethane, propane, and isobutane on Ga-doped and undoped γ -Al₂O₃. The results showed that the incorporation of Ga into γ -Al₂O₃ can reduce the C-H bond activation energy of alkane. From the kinetic point of view, it can, thus, significantly improve the activity in alkane dehydrogenation.

In the Ga/H-ZSM-5 catalyst prepared by the ion-exchange method, Cybulskis et al. [79] showed that isolated Ga ions can effectively improve the non-oxidative dehydrogenation of alkanes by promoting H₂ desorption and inhibiting catalytic cracking and other side reactions. However, due to the presence of Brønsted acid sites in zeolite, the conversion of propane to aromatic products will be improved, thereby reducing the selectivity to C₃H₆.

Lang's group [78] investigated the effects of supports (including ZSM-5, SBA-15, γ -Al₂O₃, and SiO₂) and Ga loading on the catalytic performance in propane dehydrogenation. They found that the properties of supports and Ga loading have great impact on Ga dispersion and chemical state. In particular, the strong acid sites of the support greatly promote the dispersion of Ga species but cause serious side reactions. Therefore, for Ga₂O₃-supported catalysts in propane dehydrogenation, it is crucial to balance the reaction activity, selectivity, and stability by carefully modulating their strong acid sites.

The phase structure of Ga₂O₃ has a crucial influence on the catalytic performance in the dehydrogenation of light alkanes. However, the active phases for Ga-based catalysts are still controversial, and β -Ga₂O₃, GaO⁺ ions, [GaH₂]⁺, [GaH]²⁺, etc., are all reported to be the active sites in light alkane activation [93,94]. For example, β -Ga₂O₃ is proposed to show superior activity in the initial stage of dehydrogenation, but its activity decreases rapidly (usually within 1 h). Liu et al. [95] studied the dehydrogenation of propane on β -Ga₂O₃ by the theoretical calculation method. By investigating the reaction mechanism of the C-H bond over Ga species, they found that β -Ga₂O₃ is more conducive to reduce the energy barrier. In a study of ethane dehydrogenation reaction catalyzed by stable ions (GaO⁺) in ZSM-5 zeolite, Pinko et al. [93] found that GaO⁺ ions were not the active center in light alkanes dehydrogenation on oxidized Ga/ZSM-5 zeolite, because these GaO⁺ ions were rapidly reduced to Ga⁺ ions. The author speculated that compared with the H⁺ site and thermodynamically stable Ga⁺ site, monovalent and divalent gallium hydrides, namely, [GaH₂]⁺ and [GaH]²⁺, had higher activity for the dehydrogenation reaction. Overall, [GaH]²⁺ is the most active center in the dehydrogenation of light alkanes.

Three different active centers on Ga/H-ZSM-5 catalysts with different Ga/Al ratios, including Ga⁺, Brønsted acid center, and Ga_xO_y center were reported by Lercher's group [94]. They found a synergistic effect between Ga⁺ and Brønsted acid sites in the dehydrogenation of alkanes, forming Lewis–Brønsted acid pairs. At the same concentration of the Brønsted acid and Lewis acid Ga⁺ centers, the propane dehydrogenation rate can reach the maximum. DFT calculation showed that the Lewis–Brønsted acid center could catalyze alkane dehydrogenation through the bifunctional mechanism. In this proposed mechanism, the Brønsted acid center protonated Ga⁺ to form [GaH]²⁺, which was a strong Lewis acid. [GaH]²⁺ combined with the framework oxygen of the Brønsted acid site can promote the C-H bond activation of propane, and the activation energy was only 56 kJ/mol. The activity of this Lewis–Brønsted acid pair was higher than that of isolated Ga⁺. Compared with isolated Ga⁺, the Brønsted acid sites can significantly reduce the activation energy of H₂ desorption by recombining with hydrides. Theoretical calculation proved that the heterolytic activation of the propane C-H bond happened during the reaction. These findings provide a new high-activity reaction pathway for the dehydrogenation of light alkanes (Figure 4).

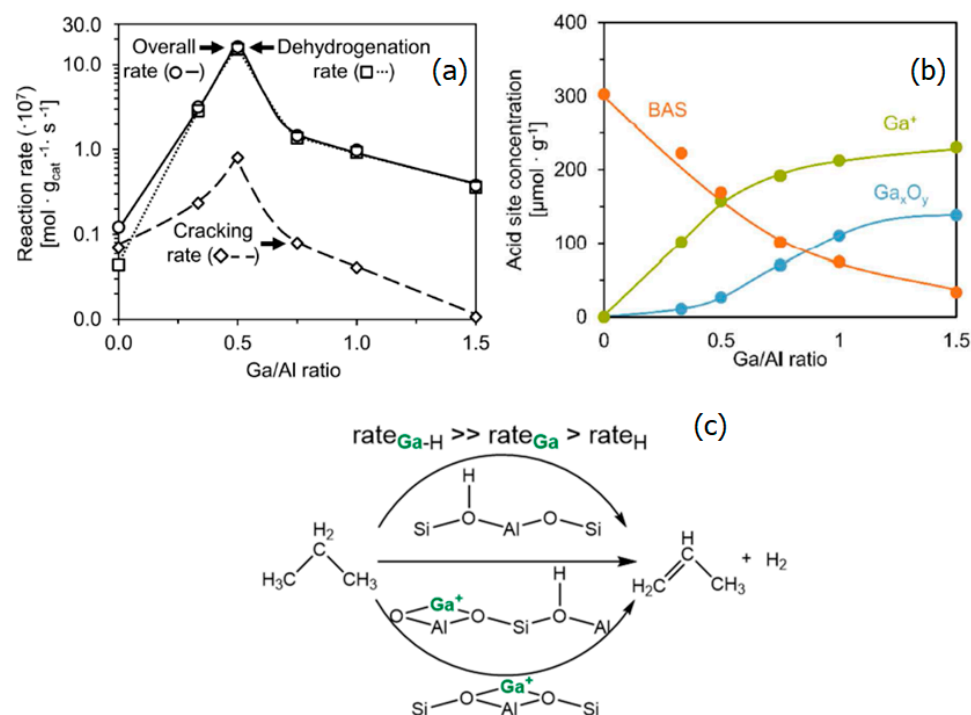


Figure 4. Influence of Ga content on reaction rate (a) and acid site concentration (b). Reaction mechanism of propane dehydrogenation over Ga-based catalysts (c). Reprinted with permission from ref. [94]. Copyright 2018 American Chemical Society.

3.2. Ga-Based Catalysts in Alkane Aromatization

Aromatic hydrocarbons, especially benzene, toluene, and xylene (BTX), as important basic chemicals in the petrochemical industry, are widely used in the pharmaceutical, food, and rubber industry. With the increasing demand, traditional fossil fuel-based routes, such as naphtha reforming, are far from enough to meet the need of BTX [96]. Therefore, the development of new routes is urgent. The dehydroaromatization of light alkanes has been widely studied in recent years due to their low cost and important strategic significance [97].

At present, some industrially available alkane aromatization processes have been reported, such as Cyclar (BP-UOP) and M2 forming. The traditional HZSM-5 zeolite is widely used in this process because of its unique shape-selective structure, which can show high selectivity to BTX. Meanwhile, to improve the activity of the catalyst and the selectivity to aromatics, dehydrogenation promoters such as Ga [34], Pt [98], and Zn [99] have been introduced. The addition of Ga species can not only improve the acidity of HZSM-5, but also play an important role in the aromatization of alkanes. This as-formed effective bifunctional Ga-based HZSM-5 catalyst can promote the conversion of light alkanes to aromatics.

A study on the mechanism of propane dehydroaromatization over Ga/HZSM-5 showed that [80] propane firstly generated propylene molecules during propane activation on Ga species and acid sites, accompanied by a cracking reaction as the side reaction. Then, propylene oligomers were quickly polymerized, and the oligomers were decomposed into light olefins afterward. The alkylation and hydrogen transfer reactions were carried on over the acidic center. These light olefins were further converted to C₆=C₈ diene, and then to aromatics through cyclization and aromatization. A lot of efforts have been made to further improve the catalytic performance of Ga/HZSM-5. For example, Xiao et al. [81] prepared Ga/HZSM-5 catalysts by continuous reduction–oxidation treatment and found that the treatment can promote the migration of Ga species from the outside surface to the inside of ZSM-5 micropores. The migrated Ga species reacted with the protons of the Brønsted acid sites and formed highly dispersed GaO⁺ species. These as-formed active species acted as strong Lewis acid sites and enhanced the dehydroaromatization of propane [100].

In another study [87], Ga/HZSM-5 catalysts with highly dispersed GaO^+ species were prepared by the formic acid-assisted impregnation method with in situ treatment (Figure 5). The propane conversion and selectivity to BTX on the as-prepared H-Ga/SNSA catalyst achieved 53.6% and 58.0%, respectively, which are significantly higher than the catalyst prepared by the traditional impregnation method (with a conversion of 38.8% and selectivity of 48.2%) when tested after 0.5 h on-stream. Moreover, the catalyst prepared by this method shows excellent BTX selectivity due to the increase of Ga species in the framework, which effectively improves the overall Lewis acid amount of the catalyst.

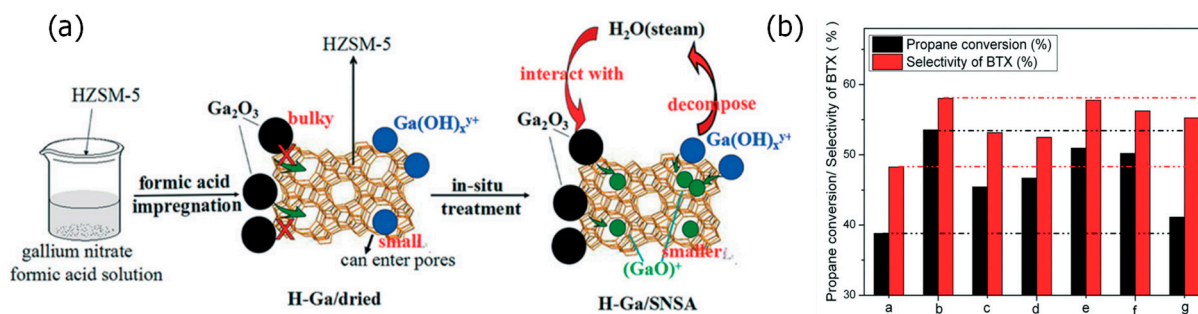


Figure 5. Ga/HZSM-5 prepared by formic acid-assisted impregnation method with in situ treatment (a), and their catalytic performance in propane aromatization (b). Reprinted with permission from ref. [87]. Copyright 2011 Royal Society of Chemistry.

Raad et al. [101] prepared three series of Ga-based catalysts by hydrothermal synthesis, ion-exchange (IE), and mechanical mixing (MM) methods. During the reduction treatment, ionic solid exchange between Ga species and the support occurred, and identical acidic and hydrogenating sites were formed on the as-prepared catalysts. In propane aromatization, the catalyst prepared by the IE method has higher coke deposition than the one with the MM method. The effects of the loading and location of Ga species, in MFI zeolite (inner and outer surfaces), on the catalytic performance were investigated. With the assistance of in situ techniques such as TPR, XPS, and FT-IR, Lewis–Brønsted acid site pair are proposed to be the active sites during aromatization reaction.

3.3. Ga-Based Catalysts in Catalytic Cracking of Alkane

Compared with steam cracking, the reaction temperature of catalytic cracking is usually lower, as in the range of 400–700 °C. With the assistance of catalysts, it is one of the most important new technical routes for light olefins production. This process can effectively reduce energy consumption and regulate product distribution. The catalytic mechanism of light alkanes cracking reaction are proposed to be the free radical mechanism, carbon ion mechanism, and free radical–carbon ion mechanism, due to the difference in catalysts and cracking conditions. HZSM-5 is an important catalyst for catalytic cracking. To further improve its catalytic performance, the construction of bifunctional catalysts with a dehydrogenation ability is one of the most important research directions. Among them, Ga species have been widely used due to their excellent catalytic performance.

Ni et al. [91] regulated different Ga species through redox atmosphere treatment, and studied the practical role of Ga species in the catalytic cracking of n-butane over Ga/ZSM-5. It was found that compared with ZSM-5, the introduction of Ga species improved the conversion of n-butane and the selectivity to light olefins and BTX. On this basis, the catalytic performance was further improved by adjusting Ga species through H_2 - O_2 treatment. The results showed that the conversion of n-butane increased from 0.53 to 2.59 $\text{mmol}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$, and the selectivity to olefins and BTX increased from 87% to 95%. Thus, a simple and industrially feasible redox treatment method was developed by a reaction and regeneration atmosphere. This study helps to deepen the understanding of the bifunctional catalytic equilibrium and is expected to provide new ideas for the design of efficient bifunctional catalysts for light alkanes conversion. In another study

of Han et al. [90], $\text{Ga}_2\text{O}_3/\text{ZSM-5}$ hollow fiber-based bifunctional catalysts were prepared by an electrostatic spinning method (Figure 6). Ga_2O_3 was used for dehydrogenation–aromatization, and ZSM-5 can serve in catalytic cracking. A very small amount of gallium can significantly improve the catalytic activity of ZSM-5. Anyway, the as-constructed hollow fiber structure can enhance the diffusion of the alkane and product molecules. Compared with $\text{Ga}_2\text{O}_3/\text{ZSM-5}$ nanoparticles, the unique hierarchical macro- and micro-structure of the as-prepared hollow fiber can effectively amplify the dual function by enhancing the accessibility of the active center and the diffusion of alkane molecules. Therefore, $\text{Ga}_2\text{O}_3/\text{ZSM-5}$ hollow fiber showed excellent n-butane catalytic cracking performance. At 600 °C, the total yield of light olefins and aromatics were the highest, which were 56.3, 24.6, and 13.3 percent higher than those of ZSM-5, ZSM-5 zeolite fibers, and $\text{Ga}_2\text{O}_3/\text{ZSM-5}$, respectively.

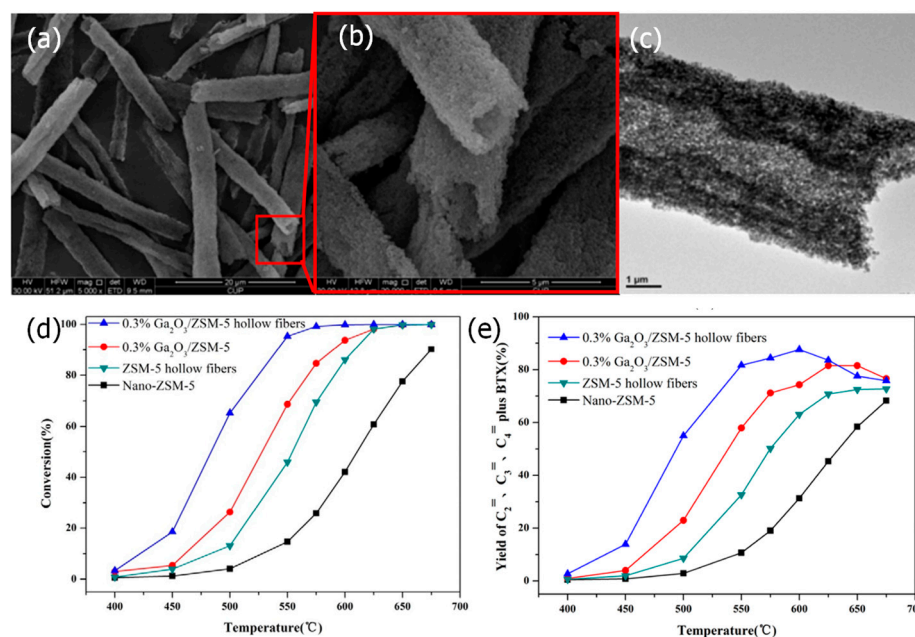


Figure 6. The low (a) and magnified (b) SEM image and TEM image (c) of $\text{Ga}_2\text{O}_3/\text{ZSM-5}$ hollow fibers. Butane conversion (d) and $\text{C}_2=\text{C}_4$ yield (e) over as-prepared Ga-based catalysts over catalytic cracking of n-butane. (Figure (b) is the magnified image of red box in figure (a)).

3.4. Ga-Based Catalysts in Alkane Isomerization

The isomerization reaction can convert alkanes into corresponding branched isomers, which is one of the important processes in the petroleum refining industry. This process has been commercialized by many companies, including UOP, ABB Lummus Global, Gulf, etc. Pt/chlorinated Al_2O_3 catalyst and some solid acids (such as sulfated zirconia) are important catalysts in alkane isomerization. To improve the catalytic performance, gallium is reported to be an efficient additive. A series of Ga-promoted sulfated zirconia-supported MCM-41 catalysts were prepared by Wang et al. [88] and introduced into a n-butane isomerization reaction. With the addition of gallium, the catalytic performance was largely improved, and the initial n-butane conversion increased from 5.17% to 43.85%. Moreno et al. [102] promoted sulfated zirconia with Al and Ga to improve the efficiency and stability of sulfated zirconia in n-butane isomerization. The stability of the tetragonal structure and the retention of sulfate in the solid were promoted. As a result, the amount of strong Brønsted acid sites was increased. It was found that the fraction of tetragonal structure and sulfate density played an important role in the activity of the catalyst. Additionally, the best catalytic performance was obtained over sulfated Ga-promoted zirconia with almost no monoclinic crystal structure and almost monolayer sulfate cover.

Liu et al. [89] prepared a series of Ga-doped ZSM-22 zeolites with uniform morphology, high crystallinity, and open pores by a hydrothermal method as the support for Pt-based isomerization catalysts. NH_3 -TPD, DMPy-IR, and Py-IR characterizations showed that the concentration of Brønsted acid center of Ga-doped ZSM-22 zeolite decreased, especially the strong Brønsted acid center at the pore. Compared with the unmodified Pt/ZSM-22 catalyst, the introduction of Ga species in the ZSM-22 greatly improved the isomerization selectivity (selectivity increased from 47.0% to 78.2% at 90% conversion) due to the more balanced bifunctionality between metal sites and acid sites. At the same time, this study also demonstrated the relationship between isomerization selectivity and Brønsted acid site distribution, indicating that the proportion of isomers can be significantly improved by reasonably adjusting the weak and strong acid sites at the pore.

These studies based on Ga as an additive provide useful perspective for the development of low-cost and simple catalysts with enhanced isomerization performance of alkanes and the realization of the clean production of lubricating oil-based inventory.

4. Conclusions

Light alkanes were converted into high value-added light olefins through different reaction pathways, which provides a new technical way for the synthesis of basic chemicals and fuels to minimize dependence on oil resources. At present, non-noble metal-based catalysts, including Ga, Sn, and Fe are bright prospects in light alkane conversion with their advantages of low costs, harmlessness, and abundant reserves. Gallium-based catalysts have been widely used in catalysis processes, such as light alkanes dehydrogenation and aromatization reaction. Due to the diversity and reducibility of Ga species, the evolution process of Ga species in the reaction process is still controversial, and research on the Ga reaction mechanism is urgently needed.

Although Ga-based catalysts have made a great impact in the field of light alkane conversion, there are still several challenges:

- (i) In future studies, the dispersion of Ga-active species on the support needs to be improved, such as modifying the preparation method and using appropriate supports. Especially with the development of preparation technology, new kinds of preparation methods can be introduced to Ga-based catalysts. The designed functional Ga catalysts can be, thus, efficiently applied and used in alkane conversion with a detailed study of their impact on Ga species modulation and metal-support interaction.
- (ii) As discussed above, Ga has many different kinds of species, which may all have catalytic activities in alkane conversion. Meanwhile, these Ga species can be changed during the reaction. Thus, the variation of Ga species during the reaction and the function of different kinds of Ga species urgently require clarification with the combination of in situ and ex situ characterizations. Additionally, the structure–catalytic performance of Ga-based catalysts should be then investigated in depth, with more studies conducted on the catalytic mechanism of Ga-based catalysts.
- (iii) Meanwhile, to further improve the catalytic performance of Ga-based catalysts, additives can be investigated. With the introduction of other components, a synergistic effect with Ga, such as electronic effect, alloy, etc., can be formed to improve its catalytic activity and stability.

Because of its environmental friendliness, abundant raw material source, and low price, gallium-based catalysts surely possess an important market value in light alkane conversion in the future.

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