Dehydrogenation of propane over spinel-type gallia–alumina solid solution catalysts

Miao Chen, Jie Xu, Fang-Zheng Su, Yong-Mei Liu, Yong Cao*, He-Yong He, Kang-Nian Fan

Department of Chemistry and Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Shanghai 200433, PR China

1. Introduction

The catalytic dehydrogenation of alkanes is a process of considerable importance, because it represents a route for obtaining alkenes from poorly reactive and low-cost saturated feedstocks [1–3]. In this respect, an important reaction is the dehydrogenation of propane to propylene [4–6]. This process is of increasing significance due to the limited capabilities of steam cracking and fluid catalytic cracking to meet the increasing demands of the propylene market [7–9]. In this sense, chromium oxide-based catalysts have been used for the dehydrogenation of propane in the absence of hydrogen as a co-feed gas [10–12], and platinum-based catalysts have been used for the dehydrogenation of propane in the presence of hydrogen [13–16]. From environmental and practical standpoints, however, chromium-free catalysts are highly desirable for the dehydrogenation of propane in the absence of hydrogen [5].

In recent years, Ga2O3-based catalysts have attracted interest as potential candidates for alkane dehydrogenation processes [5, 17–21]. This was prompted by Nakagawa’s reports of exceptionally high activity of the commercial Ga2O3 for the dehydrogenation of ethane to ethylene in the presence of CO2 [20]. Although commercial Ga2O3 has been shown to be far superior for the ethane dehydrogenation reaction compared with Cr2O3 and V2O5 catalysts, some recent studies have demonstrated that supported gallium oxides can be more active and stable for the dehydrogenation of light alkanes [5,21–23]. In particular, promising results have been obtained when the Ga2O3 catalysts are dispersed on an inert oxide support, such as TiO2 or Al2O3 [21,23], which were found to be quite active in the propane dehydrogenation reaction even at temperatures as low as 773 K [23]. Other Ga2O3-based systems evaluated in the recent literature as alkane dehydrogenation catalysts include different polymorphs of Ga2O3, such as α-, β-, γ-, and δ-Ga2O3 [24].

Despite extensive efforts dedicated to the reaction mechanism and the factors that control activity, the aforementioned Ga2O3-based catalysts all deactivate drastically within a few hours [21,23,24], because a high density of medium-strong acid sites on the surface of the Ga2O3-based materials favors considerable coke formation under alkane dehydrogenation conditions [21,23,25]. Neutralizing the acid sites by introducing potassium to the gallium oxide system has been used in propane dehydrogenation in an effort to suppress coke deposition [4]; however, this leads only to a drastic drop in catalytic activity. In the continuing search for more effective technologies for propylene production [4–6], there is a definite need for new, improved gallia-based catalysts that can allow efficient and stable dehydrogenation of propane in the presence of carbon dioxide under mild conditions.

Based on their superior ability to activate hydrocarbon species, gallia–alumina solid solutions have attracted considerable recent attention as excellent materials for the selective catalytic reduction (SCR) of NOx by hydrocarbons owing to their unique surface acidity properties [26–30]. To the best of our knowledge, however, the use of Ga2O3–Al2O3 solid solutions as catalysts in the alkane dehydrogenation reaction has not yet been reported. In the present study, we investigated the development of a new, efficient Ga2O3–Al2O3 solid solution system exhibiting significantly enhanced activity and
stability for the catalytic dehydrogenation of propane. Our results demonstrate that the formation of gallia–alumina solid solution between Ga2O3 and Al2O3 can allow the favorable creation of a higher population of surface gallium sites with weak Lewis acidity, which makes the Ga2O3-based catalysts highly active and stable for the reaction.

2. Experimental

2.1. Catalyst preparation

A series of mixed Ga2O3–Al2O3 oxide catalysts with various compositions as well as the simple oxide of Al2O3 and Ga2O3 were prepared through an alcoholic coprecipitation pathway [31]. In a typical synthesis, concentrated aqueous ammonia (28 wt%) and ethanol (50:50 in volume) was added dropwise to the ethanol solution of gallium nitrate hydrate (Aldrich, 99.99%) and aluminium nitrate hydrate (Fluka, 99.9%) with different Ga:Al molar ratio until pH ca. 8.5 and no further precipitation occurred. The resulting gel was quickly filtered and thoroughly washed by ethanol, dried at 373 K overnight, and finally calcined at 773 K for 6 h.

2.2. Catalyst characterization

The BET specific surface areas of the samples were determined by adsorption–desorption of nitrogen at liquid nitrogen temperature using a Micromeritics TriStar 3000 instrument. Powder X-ray diffraction (XRD) of the catalysts was carried out on a Germany Bruker D8Advance X-ray diffractometer using nickel-filtered Cu Kα radiation at 40 kV and 20 mA. A typical synthesis, concentrated aqueous ammonia (28 wt%) and ethanol (50:50 in volume) was added dropwise to the ethanol solution of gallium nitrate hydrate (Aldrich, 99.99%) and aluminium nitrate hydrate (Fluka, 99.9%) with different Ga:Al molar ratio until pH ca. 8.5 and no further precipitation occurred. The resulting gel was quickly filtered and thoroughly washed by ethanol, dried at 373 K overnight, and finally calcined at 773 K for 6 h.

2.3. Catalytic activity tests

Catalytic tests were performed in a fixed-bed flow microreactor at atmospheric pressure, with a catalyst load of 200 mg. Nitrogen was used as the carrier gas at a flow rate of 10 mL min⁻¹. The catalysts were pretreated at 773 K for 1 h in nitrogen flow, and the reaction temperature was 773 K. For dehydrogenation of propane in the absence of CO2, the gas reactant contained 2.5 vol% propane and the balance nitrogen (N2). For dehydrogenation of propane in the presence of carbon dioxide, the gas reactant contained 2.5 vol% propane, 5 vol% CO2, and the balance nitrogen. The hydrocarbon reaction products were analyzed with an online gas chromatograph (Type GC-122, Shanghai) equipped with a 6-m packed column of Porapak Q and a flame ionization detector. The gas products, including N2, CO, and CO2, were analyzed online by another gas chromatograph equipped with a TDX-01 column and a TCD.

2.4. Transient response of the pulsed reactions

Transient response measurements of pulsed reactions were carried out at 773 K using a U-shaped quartz reactor (4 mm i.d., 400 mm long), with 100 mg of the catalyst charged into the reactor. A pulse of propylene gas was introduced through a six-port gas-sampling valve equipped with measuring tubes under a stream of CO2 carrier gas. The signals of C1-H6 (M/e = 41), CO (M/e = 28), and H2 (M/e = 2), were recorded simultaneously by a Balzers Omnistar quadrupole mass spectrometer. Measured intensities were corrected for the relative sensitivities of the respective ions.

3. Results and discussion

3.1. Structural characterization

The powder XRD patterns of mixed Ga2O3–Al2O3 oxides with nominal Ga:Al ratios of 4:1, 1:1, and 1:4 closely resembled those of simple oxides of γ-Ga2O3 and α-Al2O3. No diffraction lines assigned to other polymorphs of Ga2O3 were observed for all mixed Ga2O3–Al2O3 oxide samples, although several phases of gallium oxide (e.g., α-, β-, and δ-Ga2O3) are known to be present depending on the treatment conditions [32]. As shown in Fig. 1, all diffraction lines were very broad, demonstrating a low crystallinity of all of the samples. This low crystallinity is a common feature of the metastable γ-variety of both alumina and gallia polymorphs [31] and was expected due to the high surface area of the mixed Ga2O3–Al2O3 samples, for which nitrogen adsorption isotherms at 77 K gave BET surface area values ranging from 119 m² g⁻¹ for the sample with a nominal Ga:Al ratio of 4:1 to 147 m² g⁻¹ for Ga:Al = 1:4 (Table 1). Within this range of end values, specific surface area was found to increase monotonously with increasing aluminum content of the mixed gallia–alumina oxides.

Despite the broadness, the diffraction maxima evidenced in the XRD patterns of the gallia–alumina samples could be assigned to a single phase having the cubic spinel-type structure (space group Fd3m) [33], as shown by the indexing in Fig. 1. The position of the diffraction angle (2θ) value was found to decrease with increasing aluminum content of the samples, thus suggesting solid solution formation [24,31,34]. From the measured d(400) spacings, corresponding values of the cubic lattice parameter, a0, were determined; these values are plotted in the inset of Fig. 1 as a function of gallium content of the mixed oxides. The a0 values of 0.790 nm for pure γ-Al2O3 and 0.832 nm for pure γ-Ga2O3 are in good accordance with the values reported in the literature [31]. The a0 value for the gallia–alumina mixed oxides showed an approximately linear dependence on the chemical composition. This result, taken together with the absence of any diffraction line not assignable to a single cubic phase in the corresponding XRD patterns, gives strong evidence of the formation of a series of spinel-type solid solutions with the chemical composition GaₙAl₁₀₋ₙO₁₅ (0 < x < 10).
XRD profiles for the Ga\textsubscript{x}Al\textsubscript{10-x}O\textsubscript{15} catalysts: (a) Ga\textsubscript{2}O\textsubscript{3}; (b) Ga\textsubscript{8}Al\textsubscript{2}O\textsubscript{15}; (c) Ga\textsubscript{5}Al\textsubscript{5}O\textsubscript{15}; (d) Ga\textsubscript{2}Al\textsubscript{8}O\textsubscript{15}; (e) Al\textsubscript{2}O\textsubscript{3}. Inset: Correlation of the lattice parameter and the chemical composition for Ga\textsubscript{x}Al\textsubscript{10-x}O\textsubscript{15}.

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>S\textsubscript{BET}\textsuperscript{a} (m\textsuperscript{2} g\textsuperscript{-1})</th>
<th>Ga/Al molar ratio</th>
<th>Ga\textsubscript{IV}\textsuperscript{d} (%)</th>
<th>Ga\textsubscript{IV\textsubscript{total}}(%)\textsuperscript{e}</th>
<th>Amount of coke\textsuperscript{f} (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ-Ga\textsubscript{2}O\textsubscript{3}</td>
<td>104 (58)</td>
<td>–</td>
<td>31</td>
<td>5.3 (4.7)</td>
<td>–</td>
</tr>
<tr>
<td>Ga\textsubscript{8}Al\textsubscript{2}O\textsubscript{15}</td>
<td>119 (102)</td>
<td>4.06</td>
<td>3.2</td>
<td>41 (3.8)</td>
<td>34 (3.8)</td>
</tr>
<tr>
<td>Ga\textsubscript{5}Al\textsubscript{5}O\textsubscript{15}</td>
<td>130 (124)</td>
<td>0.99</td>
<td>0.60</td>
<td>56 (28)</td>
<td>28 (28)</td>
</tr>
<tr>
<td>Ga\textsubscript{2}Al\textsubscript{8}O\textsubscript{15}</td>
<td>147</td>
<td>0.26</td>
<td>0.18</td>
<td>61 (13)</td>
<td>13 (13)</td>
</tr>
<tr>
<td>γ-Al\textsubscript{2}O\textsubscript{3}</td>
<td>173</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

\textsuperscript{a} The value outside and inside the bracket are the BET surface areas obtained before reaction and after three-round regeneration respectively.

\textsuperscript{b} The bulk Ga/Al molar ratio calculated from the ICP data.

\textsuperscript{c} The surface Ga/Al molar ratio based on XPS result.

\textsuperscript{d} Percentage of Ga\textsubscript{IV} calculated from the \textsuperscript{71}Ga MAS NMR results.

\textsuperscript{e} Ga\textsubscript{IV\textsubscript{total}}(\%) = \frac{n\textsubscript{Ga\textsubscript{IV}}}{n\textsubscript{Ga} + n\textsubscript{Al}} \times 100\% , \frac{n\textsubscript{Ga} + n\textsubscript{Al}}{n\textsubscript{Ga\textsubscript{IV}}} is the bulk molar ratio.

\textsuperscript{f} The value outside and inside the bracket are the amount of coke deposit of the catalysts after 8 h reaction in the absence and presence of CO\textsubscript{2} respectively.

The \textsuperscript{71}Ga MAS NMR chemical shift is known to reflect the coordination state of the Ga\textsuperscript{3+} ion in oxide compounds [31,34]. Fig. 2 shows the \textsuperscript{71}Ga MAS NMR spectra of the mixed Ga\textsubscript{2}O\textsubscript{3}–Al\textsubscript{2}O\textsubscript{3} samples and the γ-Ga\textsubscript{2}O\textsubscript{3} sample. Two asymmetric bands, split into at least four spinning sidebands, with chemical shifts of about 180 and 10 ppm [referred to Ga(NO\textsubscript{3})\textsubscript{3}] appeared in the NMR spectra of the Ga\textsubscript{x}Al\textsubscript{10-x}O\textsubscript{15} samples. According to the literature [31, 34–37], these bands are assigned to the central transition of the Ga\textsuperscript{3+} ion occupying tetrahedral (Ga\textsubscript{IV}) and octahedral (Ga\textsubscript{VI}) sites, respectively. With increasing aluminum content, a progressively increasing intensity of the line due to the tetrahedral Ga\textsuperscript{3+} ion (∼180 ppm) was observed for the Ga\textsubscript{x}Al\textsubscript{10-x}O\textsubscript{15} samples, as opposed to the trend for the octahedral Ga\textsuperscript{3+} ion (10 ppm). A peak deconvolution of the NMR Ga\textsubscript{IV} and Ga\textsubscript{VI} bands provides more information about the Ga\textsuperscript{3+} distribution (among tetrahedral and octahedral sites) in the spinel structure. As shown in Table 1, the percentage of Ga\textsuperscript{3+} ions (referred to the total Ga content of the mixed oxides) found in tetrahedral sites increased markedly with decreasing Ga/Al ratio, indicating that the Ga\textsuperscript{3+} ions preferentially occupied the tetrahedral sites of the defect spinel structure of the γ-Ga\textsubscript{2}O\textsubscript{3}–Al\textsubscript{2}O\textsubscript{3} solid solution [35–37]. The tetrahedral preference of Ga\textsuperscript{3+}, also found for many other spinels containing gallium [30, 31,38,39], can be explained in terms of a covalent contribution to the metal–oxygen bond, which is strongly developed in closed-shell d\textsuperscript{10} ions, such as Ga\textsuperscript{3+}.

### 3.2. Surface acidity measurements

The surface acidity of the mixed Ga\textsubscript{2}O\textsubscript{3}–Al\textsubscript{2}O\textsubscript{3} oxides, as well as simple oxides of γ-Ga\textsubscript{2}O\textsubscript{3} and γ-Al\textsubscript{2}O\textsubscript{3}, was measured by the NH\textsubscript{3}-TPD method. Because of the site’s low density and moderate strength, the samples were flushed with nitrogen after ammonia
Table 2
Summary of NH₃-TPD measurements

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Peak temperature (K)</th>
<th>NH₃ desorbed</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>α (393–623 K)</td>
<td>β (673–800 K)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>mmol g⁻¹cat</td>
<td>μmol m⁻²cat</td>
<td></td>
</tr>
<tr>
<td>γ-Ga₂O₃</td>
<td>480</td>
<td>754</td>
<td>4.8</td>
</tr>
<tr>
<td>Ga₈Al₂O₁₅</td>
<td>479</td>
<td>756</td>
<td>5.5</td>
</tr>
<tr>
<td>Ga₅Al₅O₁₅</td>
<td>489</td>
<td>757</td>
<td>5.0</td>
</tr>
<tr>
<td>Ga₂Al₈O₁₅</td>
<td>481</td>
<td>758</td>
<td>4.4</td>
</tr>
<tr>
<td>γ-Al₂O₃</td>
<td>493</td>
<td>758</td>
<td>3.9</td>
</tr>
</tbody>
</table>

AdSORption at a low temperature (393 K) before the TPD measurements. All of the samples exhibited two desorption peaks: a broad peak at 393–623 K and a smaller peak at 673–800 K, corresponding to acid sites of weak and medium strength, respectively [23]. The relative acid values obtained from the NH₃-TPD measurements are given in Table 2. Because no obvious relationship between the surface acidity of the oxides and the composition of the mixed oxides was observed, we correlated the specific acid site density (expressed in terms of μmol m⁻²) and the Ga³⁺ distribution based on the ⁷¹Ga NMR data. The results, given in Fig. 3, show that the weak acid site density for the gallia-alumina mixed oxides is an approximately linear function of the tetrahedral Ga³⁺ population. This result, in conjunction with much higher population of weak acid sites relative to medium sites, suggests the essential role of tetrahedral surface Ga³⁺ sites in creating the surface acidity of the mixed oxides [40,41].

Additional insight into the acid nature of the catalysts was gained from the pyridine adsorption coupled with FTIR measurements reported in Fig. 4. The results show that pyridine adsorption on fresh catalysts at room temperature, followed by evacuation at 423 K, gave rise to three characteristic IR bands at 1614 cm⁻¹ (ν₁₉a), 1490 cm⁻¹ (ν₁₉b), and ca. 1452 cm⁻¹ (ν₁₉b), which can be assigned to pyridine species interacting with Lewis acid sites [34,40,42]. According to the literature data, these Lewis acid sites are related to coordinatively unsaturated (cus) Ga³⁺ or Al³⁺ ions in the tetrahedral position [40]. No bands were observed at 1640 or 1545 cm⁻¹ in the spectra corresponding to pyridinium ions, indicating that the material under study has no Brønsted acid sites of sufficient strength to protonate the adsorbed molecule [42]. It is noteworthy that an appreciable increase in the intensity of the ν₁₉b band of adsorbed pyridine also has been identified for the mixed-oxide catalysts with respect to the simple oxide of γ-Ga₂O₃, further confirming the greater surface density of Lewis acid sites that can be achieved over the mixed-oxide materials.

3.3. Dehydrogenation of propane

The dehydrogenation of propane to propylene over the five mixed- or single-oxide catalysts in the presence or absence of CO₂ was investigated at 773 K. The major product formed in the reaction was propylene, and the minor products were ethane, ethylene, and methane. Note that the aromatization of propane occurring predominantly over Ga-ZSM-5 systems [43] was not identified in the present study, possibly due to the absence of Ga³⁺ (δ < 2) species on XPS measurements (not shown). The results, reported in Table 3, point to a marked composition effect on the catalytic performance of the GaₓAl₁₀₋ₓO₁₅ samples. The simple oxide of γ-Al₂O₃ demonstrated very low activity, consistent with the inferior activity of alumina and other metal oxides reported in the literature [20], indicating that the presence of Ga species is indispensable to the genesis of catalytically active sites for alkane dehydrogenation. For all of the Ga-containing materials, the selectivity to propylene was always high (>91%), whereas the highest conversion of propane was 51.7%. The initial conversion of propane on the catalysts decreased in the order Ga₈Al₂O₁₅ > γ-Ga₂O₃ > Ga₅Al₅O₁₅ > Ga₅Al₅O₁₅, with the same tendency observed for the specific activity normalized by BET surface area. This demonstrates that despite its lower Ga₂O₃ content, a γ-Ga₂O₃-Al₂O₃ solid solu-
A negative effect was previously reported by Xu et al. over Al2O3-dehydrogenation of propane was not observed in all samples. Such [21,23].

Reaction data in the presence or absence of carbon dioxide Table 3

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>In the presence of CO2</th>
<th>In the absence of CO2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cpropane (%)</td>
<td>Sproplylene (%)</td>
</tr>
<tr>
<td>γ-Ga2O3</td>
<td>35.9 (17.0)</td>
<td>97.2 (98.2)</td>
</tr>
<tr>
<td>Ga8Al2O15</td>
<td>49.7 (33.1)</td>
<td>91.7 (98.0)</td>
</tr>
<tr>
<td>Ga8Al2O15</td>
<td>33.7 (28.0)</td>
<td>92.9 (97.1)</td>
</tr>
<tr>
<td>Ga2Al2O15</td>
<td>19.3 (18.0)</td>
<td>92.9 (95.0)</td>
</tr>
<tr>
<td>γ-Al2O3</td>
<td>2.2 (0.5)</td>
<td>92.5 (88.4)</td>
</tr>
</tbody>
</table>

* The value outside and inside the bracket are the data obtained at 0.25 and 8 h respectively.
* Conversion of propane.
* Selectivity to propylene.
* Specific activity normalized by BET surface area.

Fig. 5 characterizes the catalytic performance in both processes as a function of reaction time. For all of the catalysts, propane conversion decreased with increasing reaction time. Thus decreased propylene yield can be attributed to carbon deposition on the surface of Ga2O3-based materials, as suggested in previous work [24,25]. With the γ-Ga2O3 catalyst, rapid deactivation of the catalyst in both the presence and absence of carbon dioxide was seen, and conversion of propane decreased from 35.9 to 17% and from 41.3 to 11.6% within 8 h, respectively. In contrast, the propylene yields were increased markedly by the introduction of aluminum in both the presence and absence of carbon dioxide in the runs for 8 h. In addition, propane conversion of the Ga4Al10–xO15 catalysts at steady state were considerably higher in the presence of carbon dioxide than in the absence of carbon dioxide, indicating remarkable stability as a function of time on stream. The amounts of coke deposited on the four Ga-containing catalysts in both processes evaluated by TGA, given in Table 1, indicate that the markedly enhanced stability of the Ga4Al10–xO15 catalysts in the presence of CO2 may be due to their low coking tendency as a function of time on stream, which appears to be rather unique in this type of application.

Previous investigations of the use of Ga2O3-based catalysts for ethane or propane dehydrogenation have found that various parameters, including the nature of the support, the coordination state and reducibility of gallium species, and the acid/base properties and gallium content of the catalysts, must be considered to account for the observed catalytic behavior in the dehydrogenation of light alkanes [4,21–25]. Generally, a catalyst with a high surface acid site density performs better in the dehydrogenation of alkanes [24]. To clarify the dependence of the catalytic activity on incorporation of aluminum, Fig. 6 illustrates the correlation between the initial activity of the Ga4Al10–xO15 catalysts in the presence of CO2 and the density of both weak and medium-strong acid sites as determined by NH3-TPD. Whereas the variation of surface weak acid site density demonstrated excellent correlation with the corresponding propane conversion rates, a negative correlation was identified between activity and medium-strong acid site density. This indicates that weak surface acidity (specifically, weak Lewis acid site density of the surface), not medium-strong surface acidity, is crucial to achieving high activity and stability. This result,
along with the essential nature of tetrahedral Ga$^{3+}$ population in contributing to weak surface acidity, provides strong evidence of the key role of surface tetrahedral Ga$^{3+}$ sites in propane dehydrogenation.

The participation of surface Ga$^{3+}$ Lewis sites in gallia-based catalysts for hydrocarbon activation has been reported [30]. In this context, it has been suggested that hydrocarbon activation proceeds on low-coordinated Ga$^{3+}$ cations, which may play a role in the chemical activation of propane by proton abstraction, leading to the formation of propyl-gallium adspecies [23,24]. The dehydrogenation products are formed by subsequent decomposition of the resulting propyl-Ga species. A recent spectroscopic investigation by Kazansky et al. [44] found that the low-coordinated Ga$^{3+}$ Lewis sites over gallium oxide were highly effective in the heterolytic dissociative adsorption of ethane even at room temperature. This unusual alkane activation behavior was linked to a very strong polarizability of the C–H bonds resulting from perturbation of ethane by the low-coordinated Ga$^{3+}$ cations [44]. This may well account for the markedly improved propane dehydrogenation activity of the Ga$_2$O$_3$-Al$_2$O$_3$ solid solution materials compared with simple gallium oxide. In this respect, it appears that more active catalysts for propane dehydrogenation can be obtained by achieving a higher population of low-coordinated surface Ga$^{3+}$ sites in the Ga$_2$O$_3$-based catalysts.

### 3.4. Stability and regeneration test

One of the main problems when using Ga$_2$O$_3$-based catalysts in the dehydrogenation of propane is their deactivation with time on stream [25]. To examine the likely long-term behavior of the gallia–alumina solid solution catalysts under reaction conditions, an extended 50-h on-stream operation for dehydrogenation of propane in the presence of CO$_2$ was carried out on the Ga$_5$Al$_5$O$_{15}$ and γ-Ga$_2$O$_3$ catalysts. As shown in Fig. 7, despite the presence of CO$_2$, rapid deactivation of the catalyst performance was observed for the simple oxide of γ-Ga$_2$O$_3$. After 16 h, propane conversion decreased significantly, to 21%. This significant decrease in propane conversion is consistent with the poor stability of Ga$_2$O$_3$-based catalysts reported in the literature [24]. Compared with the γ-Ga$_2$O$_3$ catalyst, the Ga$_5$Al$_5$O$_{15}$ sample exhibited significantly enhanced stability despite being slightly inferior to γ-Ga$_2$O$_3$ at the initial stage of the reaction. The Ga$_5$Al$_5$O$_{15}$ catalyst deactivated from an initial propane conversion value of 33.7 to 26.5% after 16 h on stream, corresponding to an activity loss of 17.2%. This loss of activity compares favorably with that of 94% for γ-Ga$_2$O$_3$ from an initial conversion of 35.9 to 2.1% after the same period of operation. It is noteworthy that even after 50 h on stream, high conversion of propane (up to 22.5%) was still maintained for Ga$_5$Al$_5$O$_{15}$. To the best of our knowledge, simple Ga$_2$O$_3$ as a dehydrogenation catalyst is inclined to deactivate rapidly, a problem that needs to be addressed [21,24]. Remarkable stability for propane dehydrogenation was recently reported for an HZSM-5-supported Ga$_2$O$_3$ catalyst at 873 K, but at the expense of marked side reactions, such as propane aromatization [25]. With high selectivity to propylene, such outstanding stability for the gallia-containing catalysts has never before been reported.

To gain more insight into the dehydrogenation of propane in the presence of CO$_2$ over Ga$_5$Al$_{10-x}$O$_{15}$ catalysts, a pulsed reaction technique was used to measure propylene adsorption over the catalyst [21]. Fig. 8 shows the transient response of propylene adsorption over various Ga$_2$O$_3$-based catalysts against a pulsed introduction of propylene at 773 K under a steady flow of CO$_2$. Nearly the same response of propylene with a similar propylene area relative to the blank runs was observed for the Ga$_5$Al$_5$O$_{15}$ catalyst; however, the propylene response was lower for the γ-Ga$_2$O$_3$, Ga$_8$Al$_2$O$_{15}$, and Ga$_5$Al$_5$O$_{15}$ catalysts than for the blank runs. In addition, the higher the gallium content, the smaller the propylene signals. It is interesting to note that although the simple oxide γ-Ga$_2$O$_3$ catalyst is characterized by a lower surface Lewis acidity, as evidenced by the NH$_3$-TPD and pyridine adsorption measurements, the desorption of propylene from the catalyst surface appeared to be favored on the surface of the gallia–alumina mixed oxide catalysts. Although more work is needed to clarify the unusual adsorption behavior of propylene on the weak surface Lewis acid sites, we believe that factors other than surface acidity, such as competitive adsorption due to the presence of CO$_2$, may play a role in determining the unique adsorption capability of the Ga–Al mixed oxide materials. Therefore, in conjunction with the coking formation data derived from TGA of the spent catalyst (Table 1), the results seem to indicate that the increased desorption of propylene from the catalyst surface is responsible for enhanced stability of the Ga$_5$Al$_{10-x}$O$_{15}$ catalysts during the catalytic dehydrogenation of propane [45–47].

Another issue of practical importance is the stability of the dehydrogenation catalyst after repeated regeneration cycles. Attempts were made to regenerate the deactivated γ-Ga$_2$O$_3$, Ga$_5$Al$_5$O$_{15}$, and Ga$_5$Al$_5$O$_{15}$ catalysts subjected to 8 h of reaction in the absence of
CO\textsubscript{2} by recalcinating the used catalyst in flowing air at 823 K for 4 h, followed by subsequent purging with N\textsubscript{2}. This procedure was found to be sufficient to burn off all carbon species deposited on the deactivated catalysts. As shown in Fig. 9, the Ga\textsubscript{5}Al\textsubscript{5}O\textsubscript{15} catalyst was much more stable than the other two samples. Clearly, the original activity of the Ga\textsubscript{5}Al\textsubscript{5}O\textsubscript{15} catalyst could be fully restored, with no noticeable deactivation detected even after the second regeneration. The Ga\textsubscript{8}Al\textsubscript{2}O\textsubscript{15} catalyst was deactivated from an initial conversion value of propane of 51.7% at 773 K to 45.5% after two successive reaction–regeneration cycles, corresponding to an activity loss of 11.9%. This loss of activity compares favorably with that of \(\gamma\)-Ga\textsubscript{2}O\textsubscript{3}, which exhibited poor aging properties in terms of a 26.9% loss from the initial steady conversion of 41.3 to 30.2% after completing the cycling process.

Given the thermally metastable nature of the \(\gamma\)-type gallium oxide materials [32,34,48], to gain further insight into the affect of repeated regeneration on the phase structure in relation to the catalytic behavior of the mixed Ga\textsubscript{2}O\textsubscript{3}–Al\textsubscript{2}O\textsubscript{3} oxides, the phase structure of the twice-regenerated catalysts (Fig. 9) was evaluated by XRD, as shown in Fig. 10. For the \(\gamma\)-Ga\textsubscript{2}O\textsubscript{3} sample, the major
phase after repeated regeneration was confirmed to be $\beta$-Ga$_2$O$_3$, which is the only stable form of Ga$_2$O$_3$ known [32,34,48]. Along with such significant phase transformation, the BET surface area of the $\gamma$-Ga$_2$O$_3$ sample also dropped dramatically to 58 m$^2$ g$^{-1}$ (as shown in Table 1), which may explain the poor performance of the simple oxide of $\gamma$-Ga$_2$O$_3$ after repeated regeneration cycles. It is noteworthy that for Ga$_{5}$Al$_{5}$O$_{15}$, no significant differences were seen in the diffraction patterns obtained before (Figs. 1b, 1c) and after (Figs. 10b, 10c) the repeated regeneration, demonstrating the improved thermal stability achievable over the mixed Ga$_2$O$_3$–Al$_2$O$_3$ oxide materials. The maintenance of the $\gamma$-phase of the solid solution materials on repeated thermal treatment is further supported by the $N_2$ adsorption data given in Table 1. Although repeated regeneration led to a general decrease in the specific surface area, higher surface areas (>100 m$^2$ g$^{-1}$) were always found for the mixed-oxide materials. Similar improved thermal stability was reported by Horiiuchi et al. for alumina–gallia aerogel materials [49]. Thus, it can be concluded that the remarkable heat-tolerant nature of the Ga$_2$O$_3$–Al$_2$O$_3$ materials with favorable surface and textural properties is responsible for these materials’ superior activity and stability in propane dehydrogenation.

4. Conclusion

The present work studied the catalytic dehydrogenation of propane in the presence or absence of CO$_2$ over a series of Ga$_{10-x}$Al$_x$O$_{15}$ mixed oxides. Among the various compositions of Ga$_{10-x}$Al$_x$O$_{15}$, the maximum initial activity and propylene yield were observed at $x = 8$. The most interesting finding of this study is the significantly enhanced stability at high conversion levels for Ga$_{5}$Al$_{5}$O$_{15}$. The enhanced catalytic activity of Ga$_{5}$Al$_{5}$O$_{15}$ mixed oxides can be linked to the abundant specific surface acid sites related to tetrahedral surface Ga$^{3+}$ sites resulting from the formation of Ga$_2$O$_3$–Al$_2$O$_3$ solid solution in the mixed-oxide systems. Comparing the NH$_3$-TPD results and propane dehydrogenation activity reveals that weak surface acidity (specifically, the weak Lewis acid site density of the surface), not medium-strong surface acidity, is important for achieving high activity and stability.

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