Short Communication

Sucrose-templated mesoporous $\beta$-Ga$_2$O$_3$ as a novel efficient catalyst for dehydrogenation of propane in the presence of CO$_2$

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A series of mesoporous $\beta$-Ga$_2$O$_3$ with high surface area have been prepared using eco-friendly sucrose as a non-surfactant template and studied in relation to their performance in the dehydrogenation of propane to propylene in the presence of CO$_2$. Among the four sucrose-derived samples tested, the material prepared from a sucrose/Ga$_2$O$_3$ molar ratio of 4 achieved the highest propane conversion, which was approximately the double efficiency of the conventional $\beta$-Ga$_2$O$_3$. The enhanced activity of the sucrose-derived materials is attributed to a high abundance of coordinative unsaturated surface Ga sites as a consequence of their favorable textural properties and enhanced surface areas.

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1. Introduction

Direct conversion of light alkanes to value-added olefins by on-purpose olefin technologies may become a potentially economically viable route in the coming years [1]. In this connection, much recent attention has been directed to the CO$_2$-mediated propane dehydrogenation (PDH), which is a potentially attractive alternative approach to produce propylene, an important monomeric feedstock in the chemical industry [2,3]. In this valuable transformation, cheap and abundant CO$_2$ serves two distinct functions: as a mild oxidant to shift the equilibrium towards products and the suppression of coke deposition [4,5]. Whereas a number of catalysts have been developed for such purpose, a persistent challenge is the control of reaction kinetics to avoid rapid deactivation owing to coke formation [6]. Thus far, gallium oxides have been recognized as one kind of the most promising materials due to their excellent catalytic efficiency as compared to conventional Cr- or V-based systems [7,8]. The superior performance of the Ga$_2$O$_3$-based system for PDH has been attributed to the unique structural characteristics of coordinatively unsaturated surface (cus) Ga$^{3+}$ sites [9], which is believed to be crucial for hydrocarbon activation in CO$_2$ atmosphere [10]. However, the development of new improved catalytic system exhibiting desirable stability and activity continues to be a major challenge.

Over the years, a number of studies have established that the population of the catalytically relevant (cus) Ga species is a strong function of the surface area of Ga$_2$O$_3$ among different Ga$_2$O$_3$ polymorphs [10–12]. In this sense, one may rationalize that simply increasing the surface area of Ga$_2$O$_3$ can lead to an improvement in the PDH activity. There were however, only very few studies on the synthesis of Ga$_2$O$_3$ with enhanced surface area. In a recent study by West et al. [13], mesoporous Ga$_2$O$_3$ with a surface area up to 307 m$^2$ g$^{-1}$ has been synthesized via a nanocasting technique using mesoporous carbon (CMK) as a hard template. The problems inherent in this procedure are that it is extremely tedious and time-consuming. A urea-based hydrothermal method using polyethylene glycol (PEG) as the soft template agent has been employed for preparation of a series of mesoporous $\beta$-Ga$_2$O$_3$ nonorods, which however can only afford a very limited accessible surface area of ca. 29 m$^2$ g$^{-1}$ [14]. Alternatively, sucrose is a kind of water soluble carbon source, which has been widely employed as a simple and convenient carbon template precursor in synthesis of high surface area $\alpha$-Al$_2$O$_3$ [15,16] and ZrO$_2$ [17]. Herein, we demonstrate for the first time that, high surface area mesoporous $\beta$-Ga$_2$O$_3$ materials prepared using eco-friendly sucrose as a non-surfactant template show a significantly improved performance for catalyzing propane dehydrogenation in the presence of CO$_2$.

2. Experimental

2.1. Catalyst preparation

An appropriate amount of sucrose was dissolved in 0.25 M aqueous Ga(NO$_3$)$_3$ solution at 303 K under continuous stirring. The pH of the solution was adjusted to ca. 5 by dropwise adding of 3 M ammonia solution. After aging at 353 K for 2 h, the resulting material was oven dried at 383 K for 24 h. The thus-obtained black precursor (2 g) was then transferred into a tube furnace and was initially annealed under N$_2$ (30 mL min$^{-1}$) at 923 K for 30 min, followed by calcination at 923 K.
under flowing air (10 mL min\(^{-1}\)) for 4 h. Four sucrose-templated samples with sucrose/Ga\(_2\)O\(_3\) molar ratio at 1, 2, 4, and 8 were synthesized, denoted as \(\beta\)-Ga\(_2\)O\(_3\)-S1, \(\beta\)-Ga\(_2\)O\(_3\)-S2, \(\beta\)-Ga\(_2\)O\(_3\)-S4, and \(\beta\)-Ga\(_2\)O\(_3\)-S8, respectively. For comparison purpose, a conventional \(\beta\)-Ga\(_2\)O\(_3\) sample was prepared by calcination of gallium nitrate at 923 K for 4 h [18].

2.2. Catalyst characterization

The BET specific surface areas of the samples were determined by adsorption–desorption of nitrogen at 77 K using a Micromeritics TriStar 3000 equipment. The X-ray powder diffraction (XRD) measurements of the catalysts were carried out on a Germany Bruker D8 Advance X-ray diffractometer using nickel filtered Cu K\(\alpha\) radiation at 40 kV and 20 mA. The acidic property of each catalyst was characterized by ammonia temperature-programmed desorption (NH\(_3\)-TPD). NH\(_3\) was adsorbed at 393 K after pre-treatment at 773 K in an He stream. The desorbed NH\(_3\) in flowing He gas was quantified (NH\(_2\) fragment of mass number 16) by mass spectroscopy (Balzers OmniStar QMS 200). The morphology and microstructure were analyzed by scanning electron microscopy (SEM, Philips XL 30) and transmission electron microscopy (TEM, JEOL-2011, operated at 200 kV).

2.3. Activity measurement

Catalytic tests were performed in a fixed-bed flow microreactor at atmospheric pressure, and the catalyst load was 200 mg. Prior to the reaction, the catalysts were pretreated at 773 K for 1 h in N\(_2\) flow. The feed was at a total flow rate of 10 mL min\(^{-1}\) containing 2.5 vol.% propane, 5 vol.% CO\(_2\), and a balance of N\(_2\). The hydrocarbon reaction products were analyzed using an on-line gas chromatograph (Type GC-122, Shanghai) equipped with a 6-m packed column of Porapak Q and a flame ionization detector (FID). The permanent gaseous products, including N\(_2\), CO, and CO\(_2\), were analyzed on-line by another GC equipped with a TDX-01 column and a thermal conductivity detector (TCD).

3. Results and discussion

It is known that gallium oxide has five different polymorphs (\(\alpha\), \(\beta\), \(\gamma\), \(\delta\), and \(\epsilon\)-Ga\(_2\)O\(_3\)), among which \(\beta\)-Ga\(_2\)O\(_3\) can be obtained by heating any other form of Ga\(_2\)O\(_3\) or gallium hydrates in air with temperature above 1173 K [19]. The diffraction profiles for the sucrose-derived Ga\(_2\)O\(_3\) samples along with conventional \(\beta\)-Ga\(_2\)O\(_3\) are shown in Fig. 1. The characteristic peaks of \(\beta\)-Ga\(_2\)O\(_3\) (JCPDS card: no. 41-1103) are

![Fig. 1. XRD profiles of various \(\beta\)-Ga\(_2\)O\(_3\) samples.](image)

![Fig. 2. Nitrogen adsorption–desorption isotherms (a) and pore size distributions (b) for Ga\(_2\)O\(_3\) samples: (■) \(\beta\)-Ga\(_2\)O\(_3\); (□) \(\beta\)-Ga\(_2\)O\(_3\)-S1; (●) \(\beta\)-Ga\(_2\)O\(_3\)-S2; (▽) \(\beta\)-Ga\(_2\)O\(_3\)-S4; and (▲) \(\beta\)-Ga\(_2\)O\(_3\)-S8.](image)

### Table 1

Summary of texture properties and NH\(_3\)-TPD measurements.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>(S_{\text{BET}}) (m(^2) g(^{-1}))</th>
<th>(V_p) (cm(^3) g(^{-1}))</th>
<th>Desorption peak temperature (K)</th>
<th>NH(<em>3) desorbed (mmol g(</em>{\text{cat}})(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\beta)-Ga(_2)O(_3)</td>
<td>38</td>
<td>0.08</td>
<td>563</td>
<td>0.46</td>
</tr>
<tr>
<td>(\beta)-Ga(_2)O(_3)-D(^a)</td>
<td>35</td>
<td>0.07</td>
<td>565</td>
<td>0.16</td>
</tr>
<tr>
<td>(\beta)-Ga(_2)O(_3)-S1</td>
<td>65</td>
<td>0.10</td>
<td>565</td>
<td>0.87</td>
</tr>
<tr>
<td>(\beta)-Ga(_2)O(_3)-S2</td>
<td>89</td>
<td>0.13</td>
<td>566</td>
<td>1.03</td>
</tr>
<tr>
<td>(\beta)-Ga(_2)O(_3)-S4</td>
<td>98</td>
<td>0.17</td>
<td>570</td>
<td>1.44</td>
</tr>
<tr>
<td>(\beta)-Ga(_2)O(_3)-S4-D(^a)</td>
<td>92</td>
<td>0.15</td>
<td>569</td>
<td>0.93</td>
</tr>
<tr>
<td>(\beta)-Ga(_2)O(_3)-S8</td>
<td>95</td>
<td>0.17</td>
<td>571</td>
<td>1.27</td>
</tr>
</tbody>
</table>

\(^a\) \(\beta\)-Ga\(_2\)O\(_3\)-D and \(\beta\)-Ga\(_2\)O\(_3\)-S4-D stand for \(\beta\)-Ga\(_2\)O\(_3\) and \(\beta\)-Ga\(_2\)O\(_3\)-S4 after reaction for 8 h on stream respectively.
observed for all samples, demonstrating that the most stable form of Ga$_2$O$_3$ was achieved via the sucrose-template synthesis. The sucrose-derived $\beta$-Ga$_2$O$_3$ samples show obviously lower crystallinity, as reflected from their broadened peaks and decreased diffraction signals relative to that for conventional $\beta$-Ga$_2$O$_3$. In general, the crystallinity for the five samples decreased in the following order: $\beta$-Ga$_2$O$_3$ > $\beta$-Ga$_2$O$_3$-S1 > $\beta$-Ga$_2$O$_3$-S2 > $\beta$-Ga$_2$O$_3$-S4 > $\beta$-Ga$_2$O$_3$-S8.

The corresponding nitrogen adsorption–desorption isotherms and pore size distributions of the Ga$_2$O$_3$ samples are presented in Fig. 2. All samples show typical type IV isotherms characteristic of mesoporous structures, among which H3 [20] and H1 [21] hysteresis loops were respectively identified for conventional $\beta$-Ga$_2$O$_3$ and the sucrose-derived samples. As summarized in Table 1, the sucrose-templating approach can afford the production of a series of mesoporous samples with favorable textural properties and enhanced surface areas. The fact that the resultant materials are pure white in color suggests a complete template removal during the calcination step, as confirmed from the thermogravimetry analysis (Fig S3). The SEM images of conventional

Fig. 3. SEM images of (a) $\beta$-Ga$_2$O$_3$; (b) $\beta$-Ga$_2$O$_3$-S1; (c) $\beta$-Ga$_2$O$_3$-S2; (d) $\beta$-Ga$_2$O$_3$-S4; and (e) $\beta$-Ga$_2$O$_3$-S8; and TEM images of (f) $\beta$-Ga$_2$O$_3$ and (g) $\beta$-Ga$_2$O$_3$-S4.
β-Ga2O3 and sucrose-derived samples are shown in Fig. 3. It is observed that conventional β-Ga2O3 presents a solid bulk structure, while the sucrose-templated samples display distinct sponge-like morphology, a feature probably as a result of the carbon template removal during combustion processing. Note that the sample prepared with higher sucrose/Ga2O3 ratio possesses higher porosity. Moreover, the TEM analysis reveals a much smaller average particle size of β-Ga2O3-S4 (Fig. 3g) relative to that of the conventional β-Ga2O3 (Fig. 3f), in line with the microstructural crystallinity as reflected from the XRD measurements.

Surface acidity of these Ga2O3 samples was measured by NH3-TPD experiments. A broad asymmetric NH3 desorption peak is registered in the TPD profiles for all five samples as shown in Fig. S1, consistent with the results observed by Zheng et al. [18]. The peak temperatures of the five samples are all located within 560–575 K, indicating the presence of only marginal variation in the acid strength for all samples. Nonetheless, there is a significant difference in the total amounts of the surface acidity between the two types of β-Ga2O3 samples. Specifically, the total acidity of the four sucrose-derived samples is approximately 1–2 times higher than that of the conventional β-Ga2O3 (Table 1). Previous studies on the surface property of β-Ga2O3 have revealed that the Lewis acid centers comprise mainly the structurally defective Ga sites characteristics of cus nature [9,22]. Thus, it follows that the remarkably increased acid sites of the sucrose-derived samples can be largely attributed to a higher density of surface defects as a consequence of the decreased crystallinity and structural modification as inferred from XRD and TEM studies.

The dehydrogenation of propane over the β-Ga2O3 samples in the presence of CO2 was investigated at 773 K, and the catalytic activity and product selectivity data were shown in Fig. 4. The major product formed in the reaction is propylene, with the minor products being ethane, ethylene, and methane. During the 8 h run, the selectivities of propylene remain above 86% for the five catalysts (Fig. 4), among which slightly higher values were achieved over the templated samples. It is interesting to note that the sucrose-derived samples gave consistently higher propane conversion during the reaction, showing that the textural properties of the β-Ga2O3 materials play a significant role in the titled reaction. Worth mentioning is that over β-Ga2O3-S4 with the highest specific surface area, a conversion of propane (43.7%) approximately twice that of conventional β-Ga2O3 (23.8%) can be achieved. As far as we are aware, this value compared favorably with the exceptionally high activity obtained with the Ga2O3-Al2O3 solid solutions [23]. It is also found that the catalytic performance show an excellent correlation with the surface acidity data (Fig. S2). Therefore, in line with the broad literature documenting the PDH reaction over Ga-based materials, it appears that a high abundance of surface Lewis acid Ga sites is the key factor in achieving high catalytic activity of sucrose-derived Ga2O3 catalysts [11,22].

As far as the stability is concerned, after 8 h run, conventional β-Ga2O3 lost 79% of its initial activity, while the sucrose-templated samples show conversion loss corresponding to 43–56% of their initial values. This reveals another attractive advantage of the sucrose-templated samples for prolonging the lifetime of β-Ga2O3 catalyst. However, deactivation is still severe for the sucrose-templated samples, and regeneration therefore seems indispensable from the perspective of application. Note that such deactivation could be largely ascribed to the blocking of the active Lewis acid sites by carbon deposition, rather than a significant degradation of the textural or structural properties of the mesoporous β-Ga2O3-S4 material (Table 1). For regenerating β-Ga2O3-S4 that reacted 8 h on stream at 773 K, the reaction was interrupted under an N2 stream, and then air was introduced at 923 K to burn off carbon species deposited on the catalyst (Fig. 5). After the first regeneration, the initial propane conversion for β-Ga2O3-S4 amounted to 39% at 773 K, which is slightly lower than that for the fresh sample (43.7%). However, after the second and third regenerations, only marginal variations in initial activity were observed. Analogous phenomenon was reported by Zheng et al. in regeneration of β-Ga2O3 [18].

4. Conclusions

The present work demonstrates the high potential of using environmentally friendly sucrose as a non-surfactant template to prepare mesoporous β-Ga2O3 materials with favorable textural and structural properties for the dehydrogenation of propane with CO2. It is important to highlight here that this approach is not limited to the use of sucrose as the carbohydrate-based carbon sources (see Table S1). The present findings may provide new opportunities for the rational design of new mesostructured gallium oxide catalyst systems for advanced applications.
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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2012.11.004.

REFERENCES


Fig. 5. Regeneration tests of β-Ga2O3-S4 catalyst.