

Enhanced Activity of Spinel-type Ga₂O₃–Al₂O₃ Mixed Oxide for the Dehydrogenation of Propane in the Presence of CO₂

Miao Chen · Jie Xu · Yong-Mei Liu · Yong Cao ·
He-Yong He · Ji-Hua Zhuang · Kang-Nian Fan

Received: 17 February 2008 / Accepted: 17 March 2008 / Published online: 25 March 2008
© Springer Science+Business Media, LLC 2008

Abstract Catalytic performance of a series of Ga₂O₃–Al₂O₃ mixed oxides prepared by alcoholic-coprecipitation method for the dehydrogenation of propane in the presence of CO₂ was investigated. It is shown that the combination of Ga and Al oxides greatly improved the performance of the Ga₂O₃-based materials for catalytic dehydrogenation of propane, with the highest performance attainable at a Ga₂O₃–Al₂O₃ catalyst with a 20 mol% aluminum content. While the same tendency was observed for the specific activity normalized by BET surface area, significantly enhanced stability was achieved for Ga₂O₃–Al₂O₃ with higher aluminum content. X-ray diffraction (XRD) revealed that a homogeneous spinel-type Ga₂O₃–Al₂O₃ solid solution is uniformly formed by substitution of Ga³⁺ for Al³⁺ in the Al₂O₃ lattice. The enhanced activity of Ga₂O₃–Al₂O₃ mixed oxides was accounted for by the abundance of surface weak acid sites due to the synergetic interaction between Ga₂O₃ and Al₂O₃ in the solid solution systems.

Keywords γ -Ga₂O₃ · γ -Al₂O₃ · Solid solution · Dehydrogenation · Propane · Propylene

1 Introduction

The increasing need of upgrading low-cost feedstocks has greatly prompted the research on the use of light alkanes as

an alternative to the production of the more expensive olefins [1, 2]. In this sense, much attention has been recently paid to the catalytic dehydrogenation of alkanes to give the corresponding alkenes, which is of increasing significance due to the limited capacities from steam cracking and fluid catalytic cracking [3, 4]. Chromia- or platinum-based catalysts have been found to be active and selective for this process [5–9]. Especially in the field of the catalytic dehydrogenation of propane to propylene, it has been well established that these catalysts are frequently susceptible to rapid deactivation owing to coking formation under severe operating conditions [10, 11]. Thus, new efficient catalyst systems that can allow the effective transformation of propane at lower temperatures are highly desirable.

In recent years, gallium oxide-based catalysts have attracted considerable attention as new promising alkane dehydrogenation materials owing to their unique capability to activate hydrocarbon species under mild conditions [12–18]. This was prompted by Nakagawa's discovery of exceptionally high activity of the commercial Ga₂O₃ for the dehydrogenation of ethane to ethylene in presence of CO₂ [12]. Although featured with a very low surface area (<10.0 m²/g), commercial Ga₂O₃ has been found to be far superior for the ethane dehydrogenation reaction compared to Cr₂O₃- and V₂O₅-based catalysts [12]. Subsequent studies by evaluating different polymorphs of Ga₂O₃ have revealed that β -Ga₂O₃ is more effective in terms of the specific activity for propane dehydrogenation with respect to its other polymorphic counterparts [19]. Along this line, several recent studies have shown that supported gallium oxides could be more active and stable to the dehydrogenation of light alkanes [15–21]. In particular, promising results have been obtained when the Ga₂O₃ catalysts are dispersed on inert oxide supports such as TiO₂ or Al₂O₃

M. Chen · J. Xu · Y.-M. Liu · Y. Cao (✉) · H.-Y. He ·
J.-H. Zhuang · K.-N. Fan
Department of Chemistry & Shanghai Key Laboratory of
Molecular Catalysis and Innovative Materials, Fudan University,
Shanghai 200433, P.R. China
e-mail: yongcao@fudan.edu.cn

[20], which were found to be quite active in the propane dehydrogenation reaction even at temperatures as low as 773 K.

In the present work, we report the development of new efficient $\text{Ga}_2\text{O}_3\text{--Al}_2\text{O}_3$ mixed oxide system exhibiting significantly enhanced activity and stability for the catalytic dehydrogenation of propane in the presence of CO_2 . The gallia–alumina solid solution, previously established to be an effective material for the selective catalytic reduction (SCR) of NO_x by hydrocarbons [22, 23], has shown to be particularly useful in regulating the structural and surface acidity properties of the $\text{Ga}_2\text{O}_3\text{--Al}_2\text{O}_3$ mixed oxide catalysts for the catalytic dehydrogenation of propane. Our results have shown that the formation of gallia–alumina solid solution between Ga_2O_3 and Al_2O_3 can allow the favorable creation of a higher population of surface gallium sites with relatively weak acidity, which makes the catalysts highly active and stable for the reaction.

2 Experimental

2.1 Catalyst Preparation

A series of $\text{Ga}_2\text{O}_3\text{--Al}_2\text{O}_3$ mixed oxide catalysts with various compositions as well as the simple oxide of Al_2O_3 and Ga_2O_3 were prepared through an alcoholic coprecipitation pathway [24]. In a typical synthesis, concentrated aqueous ammonia and ethanol (50:50 in volume) was added dropwise to the ethanol solution of gallium nitrate hydrate (Aldrich, 99.99%) and aluminum nitrate hydrate (Fluka, 99.9%) with different Ga:Al molar ratio until no more precipitation occurred. The resulting gel was quickly filtered and washed by ethanol, and dried at 373 K for overnight, and finally calcined at 773 K for 6 h. The obtained mixed oxide samples were annotated according to their nominal compositions, i.e., GaAl-4/1, GaAl-1/1 and GaAl-1/4 stand for $\text{Ga}_2\text{O}_3\text{--Al}_2\text{O}_3$ mixed oxide catalysts with Ga/Al molar ratio of 4:1, 1:1 and 1:4 respectively.

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 equipment. The X-ray powder diffraction (XRD) of the catalysts was carried out on a Germany Bruker D8Advance X-ray diffractometer using nickel filtered $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) at 40 kV and 20 mA. The acidic property of each catalyst was characterized by $\text{NH}_3\text{-TPD}$. NH_3 was adsorbed at 393 K after pre-treatment at 773 K in a He stream. The desorbed NH_3 in flowing He gas was quantified (NH_2 fragment of mass number 16) by mass

spectroscopy (Balzers OmniStar) at temperatures from 393 to 873 K at a ramp rate of 10 K/min. Elemental analysis was performed using ion-coupled plasma (ICP) atomic emission spectroscopy on a Thermo Electron IRIS Intrepid II XSP spectrometer. Thermal gravimetric analysis (TGA) was conducted on a Perkin-Elmer TGA-7 apparatus to determine the amount of coke deposited on the catalyst after the reaction. Twenty milligrams of sample was heated from room temperature to 873 K at a heating rate of 10 K/min in flowing air.

2.3 Catalytic Activity Measurements

Catalytic tests were performed in a fixed-bed flow microreactor at atmospheric pressure, and the catalyst load was 200 mg. Nitrogen was used as the carrier gas at a flow rate of 10 mL/min. The catalysts were pretreated at reaction temperature for 1 h in nitrogen flow prior to reaction. During the dehydrogenation process, the gas reactant contained 2.5 vol% propane, 5 vol% carbon dioxide, and a balance of nitrogen. 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. The gas products, including N_2 , CO, and CO_2 , were analyzed on-line by another chromatograph equipped with a TDX-01 column and a TCD.

3 Results and Discussion

3.1 Catalytic Dehydrogenation of Propane

The catalytic dehydrogenation of propane to propylene over $\text{Ga}_2\text{O}_3\text{--Al}_2\text{O}_3$ mixed oxides and two simple oxides in the presence of CO_2 was investigated at 773 K. The results, along with the specific activities normalized by BET surface area were provided in Table 1. In addition to the major product of propylene, byproducts attributed to cracking such as ethylene, ethane and methane were also detected. From the results, it can be seen that the activity was strongly dependent on the composition of the mixed oxides. The simple oxide of Al_2O_3 demonstrated a very low activity with a propane conversion of 2.2% at 0.25 h on stream. This low activity was fully in line with the inferior activity of alumina or other metal oxides as reported in the literature [12], indicating that the presence of Ga species is indispensable for the genesis of catalytically active sites for propane dehydrogenation. On the other hand, the Ga-containing materials all led to a significant production of propylene with high selectivities (>90%) and appreciable initial conversions of propane ranging from ca. 20–50%. The initial conversions of propane on the catalysts

Table 1 Physicochemical and catalytic properties of the mixed Ga₂O₃–Al₂O₃ oxides

Catalyst	BET (m ² /g)	Conversion ^a (%)	Selectivity ^a (%)				Activity ^b μmol/(h m ²)	Ga/Al molar ratio ^c	Amount of coke ^d (%)
			C ₃ H ₆	CH ₄	C ₂ H ₄	C ₂ H ₆			
Ga ₂ O ₃	104	35.9 (17.0)	97.2 (98.2)	0.6 (0.4)	1.9 (1.3)	0.3 (0.1)	12 (5.5)	–	4.7
GaAl-4/1	119	49.7 (33.1)	91.7 (98.0)	2.8 (0.7)	4.7 (1.1)	0.8 (0.2)	14 (9.3)	4.16	3.8
GaAl-1/1	130	33.7 (28.0)	92.9 (97.1)	2.9 (1.2)	3.6 (1.4)	0.6 (0.3)	8.7 (7.2)	0.99	2.1
GaAl-1/4	147	19.3 (18.0)	92.9 (95.0)	3.7 (2.7)	2.9 (1.8)	0.5 (0.5)	4.4 (4.1)	0.27	1.5
Al ₂ O ₃	173	2.2 (0.50)	92.5 (88.4)	0.8 (1.1)	3.5 (4.1)	5.2 (6.4)	0.43 (0.10)	–	–

^a The value outside and inside the bracket are the data obtained at 0.25 h and 8 h respectively

^b Specific activity normalized by BET surface area

^c The bulk Ga/Al molar ratio calculated from the ICP data

^d The values are the weight percentage of coke determined by the TG analysis of the samples reacted in the presence of CO₂ for 8 h

decreased in the order: GaAl-4/1 > Ga₂O₃ > GaAl-1/1 > GaAl-1/4, with the same tendency being observed for the specific activities. This showed that, despite a lower content of Ga₂O₃, Ga₂O₃–Al₂O₃ mixed oxide with suitable composition could be even more active than pure Ga₂O₃ in the initial stage.

Table 1 also presented the catalytic performance after 8 h on stream. For all catalysts, propane conversions underwent noticeable decrease which could be attributed to carbon deposition on the surface of Ga₂O₃-based materials, as suggested in the previous papers [19, 21]. Most drastic deactivation occurred over pure Ga₂O₃ as expected, for which after 8 h a decline of propane conversion by 18.9% corresponding to more than half of its initial activity was observed. This poor stability agrees well with the fast deactivation of the bulk oxide of Ga₂O₃ as reported in the literature [14]. In contrast, deactivation was found to be less prominent over the Ga₂O₃–Al₂O₃ mixed oxides within 8 h. From 0.25 h to 8 h, the conversion of propane decreased by 16.6, 5.7 and 1.3% for GaAl-4/1, GaAl-1/1 and GaAl-1/4, respectively, revealing a synergistic effect between Ga₂O₃ and Al₂O₃ leading to enhanced stability. Moreover, it could be observed that, after 8 h reaction period the sequence of the conversions had changed into: GaAl-4/1 > GaAl-1/1 > GaAl-1/4 > Ga₂O₃. This means that the Ga₂O₃–Al₂O₃ mixed oxides with the Ga/Al ratio ranging from 1/4 to 4/1 were all superior to Ga₂O₃ with respect to the steady-state activity, in spite of the possibly inferior performance in the initial stage.

To investigate the likely long-term stability of the Ga–Al mixed oxide catalysts under reaction conditions, an extended 20 h on-stream operation for dehydrogenation of propane in the presence of CO₂ was carried out. As shown in Fig. 1, rapid deactivation of the catalyst performance was observed for the simple oxide of Ga₂O₃. After 16 h, the propane conversion strongly decreased to 2.1%. Compared to the pure Ga₂O₃ catalyst, all mixed oxide samples exhibited enhanced stability, with such positive effect

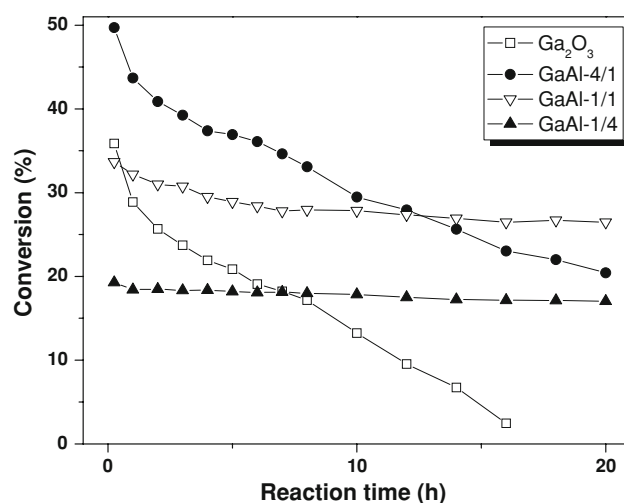


Fig. 1 Conversion of propane as a function of time on stream for Ga₂O₃, GaAl-4/1, GaAl-1/1 and GaAl-1/4 at 773 K

being more pronounced for the material with higher aluminum content. As far as sample GaAl-1/1 is concerned, despite being slightly inferior to Ga₂O₃ at the initial stage of the reaction, this catalyst exhibited remarkably enhanced stability at high conversion levels. The GaAl-1/1 catalyst deactivated from an initial conversion value of propane of 33.7 to 26.5% after 16 h on-stream operation, this corresponding to a loss in activity of 17.2%. This loss of activity compared favorably with that for catalyst Ga₂O₃ of 94% from initial conversion of 35.9 to 2.1% after the same period of operation. It is worth noting that, after 20 h on-stream operation, a high conversion of propane up to 26.5% could still be maintained for GaAl-1/1. To the best of our knowledge, Ga₂O₃ as a dehydrogenation catalyst inclined to deactivate rapidly which is a vital problem to be settled. At this situation, it is important to note that under similar reaction conditions, the Ga₂O₃/Al₂O₃ system prepared by conventional impregnation as reported by Xu et al. [20] experienced a drastic deactivation in a short time

of 6 h, probably due to the lacking of the intimate interaction of the two oxides in contrast to the present solid solution sample. Remarkable stability for propane dehydrogenation has been recently achieved for HZSM-5 supported Ga_2O_3 catalyst at 873 K [21], but unavoidable propane aromatization would also take place as side reaction. With high selectivity to propylene, such outstanding stability as to the gallia-containing catalysts has never been reported before.

The effect of the reaction temperature on the dehydrogenation activity of the most active GaAl-4/1 catalyst was examined. Propylene yield and selectivity as a function of reaction temperature are shown in Fig. 2. With increase of the reaction temperature, the propylene yield markedly increased from 7.0% at 723 K to 48.7% at 823 K, whereas the selectivity to propylene decreased from 97.1% at 723 K to 76.1% at 823 K. The decrease of the propylene selectivity could be partly attributed to the increase of the yield of by-products (methane, ethane and ethylene). The rate of deactivation of the GaAl-4/1 catalyst increases with increasing the reaction temperature and time as shown in Fig. 3. The rapid deactivation of GaAl-4/1 was observed at 823 K. After the reaction period of 8 h the propane conversion dramatically decreased from 64.0 to 21.1%. The change in propane conversion was much lower at 773 K; after 8 h the propane conversion was still as high as 33.1%. These results clearly indicated that high temperature accelerates coke deposition on the $\text{Ga}_2\text{O}_3\text{--Al}_2\text{O}_3$ catalyst surface. Taking both yield of propylene and the catalyst stability into account, 773 K could be the most appropriate

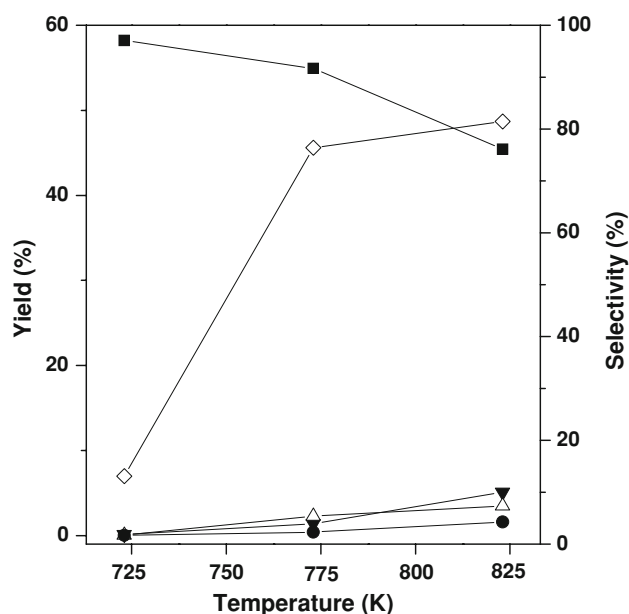


Fig. 2 Effect of reaction temperature on dehydrogenation of propane over GaAl-4/1; (■) selectivity to propylene; (□) propylene (□) methane (▼) ethylene (●) ethane yield

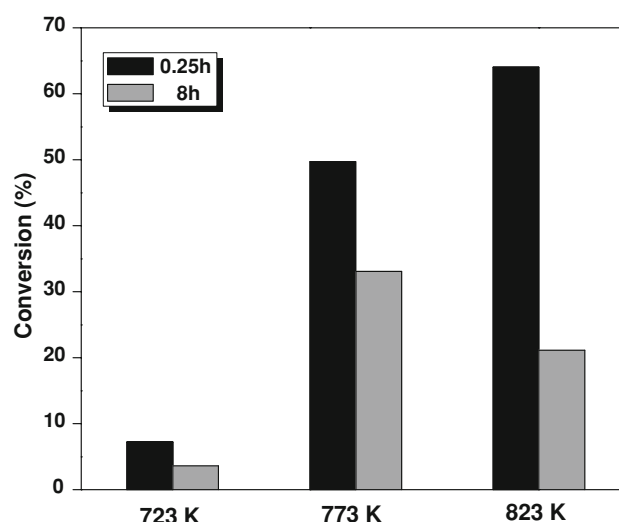


Fig. 3 Conversion of propane for GaAl-4/1 at different temperatures after the reaction times 0.25 h and 8 h

temperature for the propane dehydrogenation reaction over $\text{Ga}_2\text{O}_3\text{--Al}_2\text{O}_3$ mixed oxides.

3.2 Catalyst Characterization

Figure 4 shows the XRD patterns of the simple oxide of Al_2O_3 and Ga_2O_3 as well as the $\text{Ga}_2\text{O}_3\text{--Al}_2\text{O}_3$ mixed oxide catalysts with various compositions. It is evident that Ga_2O_3 and Al_2O_3 were all in the γ -phase, corresponding to the spinel type of structure in which Ga^{3+} or Al^{3+} ions are situated in either fourfold or sixfold coordination [22, 25]. For the mixed oxide samples, the diffraction patterns all closely resembled those of the $\gamma\text{-Ga}_2\text{O}_3$ or $\gamma\text{-Al}_2\text{O}_3$. No signal indicative of other polymorphs of Ga_2O_3 was detected, although several phases of gallium oxide, for example,

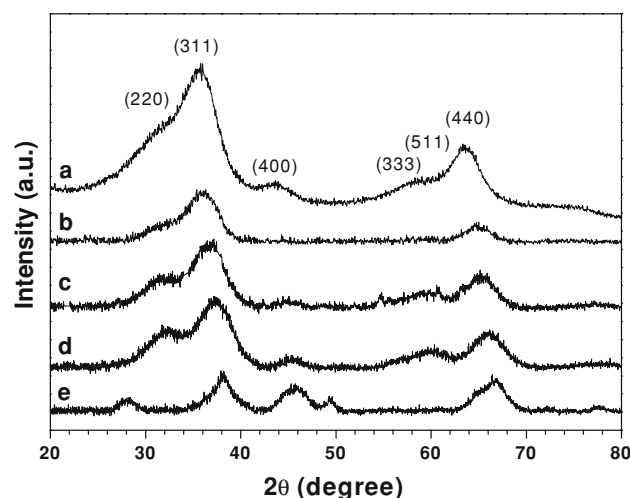


Fig. 4 XRD profiles for the $\text{Ga}_2\text{O}_3\text{--Al}_2\text{O}_3$ catalysts: (a) Ga_2O_3 ; (b) GaAl-4/1; (c) GaAl-1/1; (d) GaAl-1/4; (e) Al_2O_3

α -, β -, and δ -Ga₂O₃, are known to be present depending upon the treatment conditions [24, 25]. It also can be observed that the diffraction peaks were rather broad that suggested a poor crystallinity nature of the mixed oxide samples, which has already been reported to be a common feature of the metastable γ -variety of both alumina and gallia polymorphs [24, 25]. It was also expected as a result of 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, for the sample having a nominal Ga:Al ratio of 4:1, to 147 m²/g for Ga:Al = 1:4 (Table 1). Within these end values, specific surface area was found to increase monotonously with increasing aluminum content of the mixed gallia–alumina oxides.

Broadness notwithstanding, 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*) [24] as shown by the indexing in Fig. 4. The position of the diffraction angle was found to decrease with increasing aluminum content of the samples, thus suggesting solid solution formation. From the measured $d_{(440)}$ spacings, corresponding values of the cubic lattice parameter, a_0 , were determined [26]. These values are plotted in Fig. 5 as a function of gallium content of the mixed oxides. Note that the a_0 for pure γ -Al₂O₃ and γ -Ga₂O₃ are determined to be 0.790 and 0.832 nm, respectively, in good accordance with the values reported in literature. It is observed that a_0 for the gallia–alumina mixed oxides shows an approximately linear dependence on the chemical composition (ICP) (Table 1). This result, taken together with the absence of any diffraction line not assignable to a single cubic phase in the corresponding

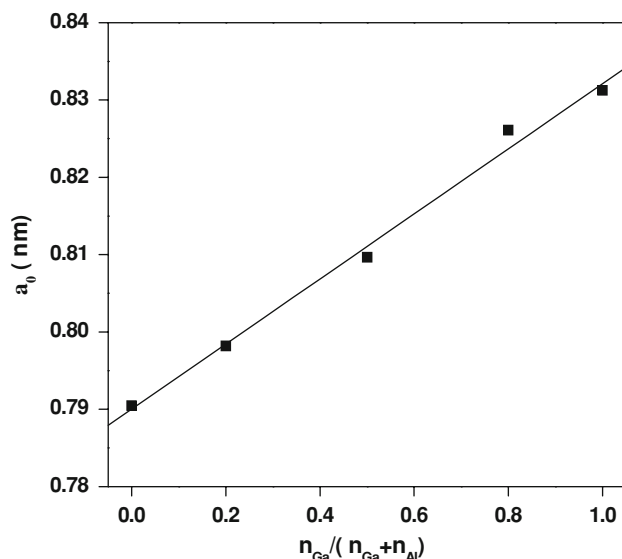


Fig. 5 Correlation of the lattice parameter and the chemical composition for Ga₂O₃–Al₂O₃ mixed oxides

XRD patterns, gives strong evidence for the formation of a series of spinel-type solid solutions having the chemical composition Ga_xAl_{2-x}O₃ ($0 \leq x \leq 2$).

The surface acidity of the mixed Ga₂O₃–Al₂O₃ oxides as well as simple oxides of γ -Ga₂O₃ and γ -Al₂O₃ was measured by the NH₃-TPD method as shown in Fig. 6. All samples displayed two desorption peaks [20]: one broad peak in the range of 393–623 K, and the other smaller peak in the range of 673–800 K, corresponding to acid sites of weak and medium strong strength, respectively. The acid site amounts obtained from the NH₃-TPD measurement were summarized in Table 2. It was obvious that the weak acid sites other than the medium strong acid sites dominated over the sample surfaces in view of the much higher amount for weak acid sites. Another important point was the different composition dependence behavior observed for these two kinds of acid sites. With weak acid sites, the amounts for the solid solution samples were higher than that for either Al₂O₃ or Ga₂O₃, suggesting not simple oxide but rather combination of the two species in the solid solutions was essential for creating high population of weak acid sites. On the other hand, the variation for medium strong acid sites showed that the amount increased approximately proportional to the Al content, suggesting no significant change took place for medium strong acid sites as Ga₂O₃–Al₂O₃ solid solutions formed. This

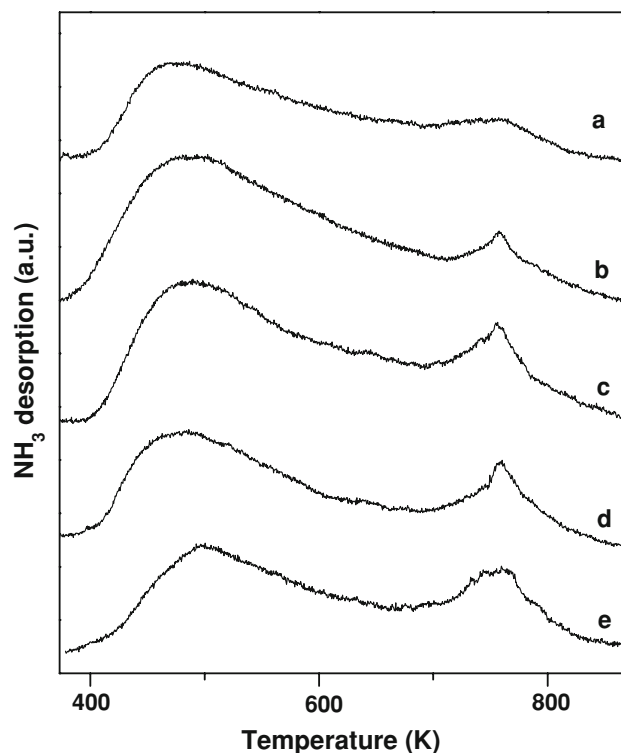


Fig. 6 NH₃-TPD profiles of the Ga₂O₃–Al₂O₃ catalysts: (a) Ga₂O₃; (b) GaAl-4/1; (c) GaAl-1/1; (d) GaAl-1/4; (e) Al₂O₃

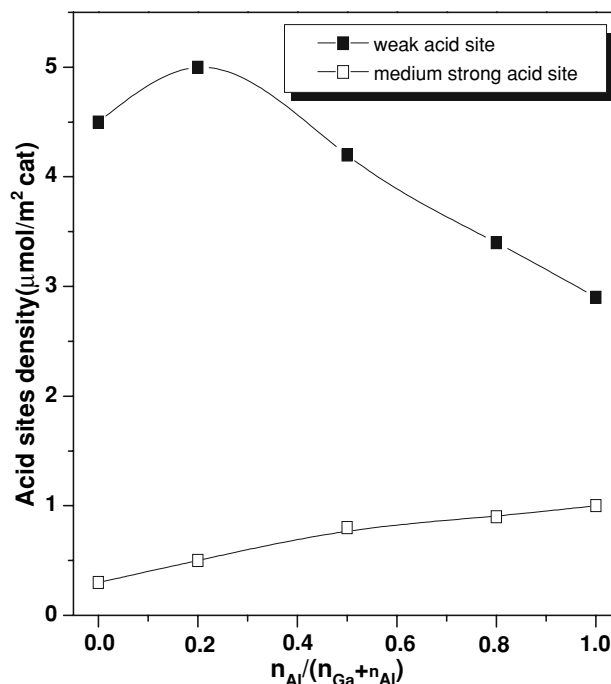
Table 2 NH₃-TPD data of the mixed Ga₂O₃–Al₂O₃ oxide samples

Catalyst	Peak temperature (K)		NH ₃ desorbed		
	α	β	α (393–623 K), mmol/g-cat	β (673–793 K), mmol/g-cat	Total, mmol/g-cat
Ga ₂ O ₃	480	754	0.47	0.03	0.50
GaAl-4/1	479	756	0.60	0.06	0.66
GaAl-1/1	489	757	0.55	0.11	0.66
GaAl-1/4	481	758	0.53	0.14	0.67
Al ₂ O ₃	493	758	0.51	0.18	0.69

comparison revealed that, the formation of solid solution contributed a lot to the creation of weak acid site, while was less relevant to the medium strong acid site.

Previous investigations concerning the use of Ga₂O₃-based catalysts for ethane or propane dehydrogenation have shown that a number of parameters such as the nature of support, coordination state and reducibility of gallium species, the acid/base properties as well as the gallium content of the catalysts have to be considered in order to account for the observed catalytic behavior for the dehydrogenation of light alkanes [14, 18–20]. Generally, catalyst with high surface acid site density shows better performance in the catalytic dehydrogenation of propane [20]. In order to clarify the dependence of the catalytic activity upon aluminum incorporation, the effect of chemical composition on the surface acid site density with either weak or medium strong strength (expressed in terms of $\mu\text{mol}/\text{m}^2$) has been comparatively illustrated in Fig. 7. While the variation of surface medium-strong acid sites density shows an almost linear increase with increasing aluminum content of the mixed gallia–alumina oxides, a maximum value of the weak surface weak acid site density was observed for Ga₂O₃–Al₂O₃ with a 20 mol% aluminum content. By correlation with the initial activity data as included in Table 1, one can see that there is a good relationship between the weak acid site density and the performance of the Ga₂O₃–Al₂O₃ samples. This indicates that not the medium-strong surface acidity, but rather weak surface acidity, specifically the weak Lewis acid site density of the surface, is important for achieving a high activity and stability. This result, taken together with the TG analysis showing pronounced inhibition of carbon deposition over the Al-doped samples (see Table 1), gives strong evidence the unique synergistic effect between Ga₂O₃ and Al₂O₃ for catalytic propane dehydrogenation.

On the other hand, it is important to note that single alumina exhibited much lower activity despite the presence of substantial amount of weak acid density as given in Fig. 7, inferring that additional factors other than weak acidity may play a role in determining the catalytic behavior of the present Ga–Al mixed oxide materials. While further work is needed to fully understand the

**Fig. 7** Correlation of acid site density and the chemical composition of Ga₂O₃–Al₂O₃ mixed oxides

mechanism of the weak Lewis site-mediated hydrocarbon activation, we believe that the presence of Ga species is indispensable for the genesis of catalytically active sites for alkane dehydrogenation. The participation of coordinative unsaturated Ga³⁺ species in gallia-based catalysts for hydrocarbon activation has been reported so far [19, 20]. In the present case of Ga₂O₃–Al₂O₃, the presence of the following three kinds of reaction sites are presumed: Al³⁺–O–Al³⁺, Ga³⁺–O–Ga³⁺ and Al³⁺–O–Ga³⁺. Because the importance of synergistic effect between Ga and Al ions was suggested as described above, Al³⁺–O–Ga³⁺ are plausible as the most active reaction sites. This may well account for the much inferior activity of alumina as compared to those Ga-containing oxide materials. In this respect, it appears that the specific surface weak acid sites comprising coordinative unsaturated Ga³⁺ species is the key factor in determining the catalytic performance of the Ga₂O₃–Al₂O₃ solid solution materials.

4 Conclusions

The Ga₂O₃–Al₂O₃ mixed oxide catalysts synthesized by alcoholic coprecipitation have been found to exhibit superior performance for the catalytic dehydrogenation of propane due to the formation of well-defined spinel-type solid solution in the Ga–Al mixed oxide materials. Combined XRD and NH₃-TPD results demonstrated that the specific interaction between Ga₂O₃ and Al₂O₃ can result in the formation of Ga₂O₃–Al₂O₃ solid solution in which the structural and surface acidity properties are substantially modified. Compared to the simple oxide of Ga₂O₃, the as-prepared Ga₂O₃–Al₂O₃ mixed oxide catalysts show particularly enhanced stability for the catalytic dehydrogenation of propane. Our results show that the highest catalytic performance can be attained at a Ga₂O₃–Al₂O₃ mixed oxide catalyst with a 20 mol% aluminum content, which allows the steady formation of a maximum propylene yield of ca. ~26% in the catalytic dehydrogenation of propane. The high catalytic activity of the present Ga₂O₃–Al₂O₃ solid solution catalysts has been attributed to the favorable creation of a higher population of surface gallium sites with relatively weak acidity in the mixed oxide catalysts.

Acknowledgments This work was financially supported by the National Natural Science Foundation of China (20421303, 20473021, 20633030), the National High Technology Research and Development Program of China (2066AA03Z336), and the National Basic Research Program of China (2003CB615807), the Shanghai Science & Technology Committee (07QH14003) and Shanghai Education Committee (06SG03).

References

1. Bettahar MM, Costentin G, Savary L, Lavalley JC (1996) *Appl Catal A* 145:1
2. Chaar MA, Patel D, Kung HH (1988) *J Catal* 109:463
3. Vitry D, Dubois J-L, Ueda W (2004) *J Mol Catal A* 220:67
4. Liu YM, Cao Y, Yi N, Feng WL, Dai WL, Yan SR, He HY, Fan KN (2004) *J Catal* 224:417
5. Kogan SB, Schramm H, Herskowitz M (2001) *Appl Catal A* 208:185
6. Zhang Y, Zhou Y, Qiu A, Wang Y, Xu Y, Wu P (2006) *Catal Commun* 7:860
7. Yu CL, Ge QJ, Xu HY, Li WZ (2007) *Ind Eng Chem Res* 46:8722
8. Gascon J, Tellez C, Herguido J, Menendez M (2003) *Appl Catal A* 248:105
9. Rombi E, Cutrufello MG, Solinas V, De Rossi S, Ferraris G, Pistone A (2003) *Appl Catal A* 251:255
10. Liu YM, Feng WL, Li TC, He HY, Dai WL, Huang W, Cao Y, Fan KN (2006) *J Catal* 239:125
11. Liu YM, Feng WL, Wang LC, Cao Y, Dai WL, He HY, Fan KN (2006) *Catal Lett* 106:145
12. Nakagawa K, Okamura M, Ikenaga N, Suzuki T, Kobayashi T (1998) *Chem Commun* 1025
13. Nakagawa K, Kajita C, Ide Y, Okamura M, Kato S, Kasuya H, Ikenaga N, Kobayashi T, Suzuki T (2000) *Catal Lett* 64:215
14. Nakagawa K, Kajita C, Okumura K, Ikenaga N-O, Nishitani-Gamo M, Ando T, Kobayashi T, Suzuki T (2001) *J Catal* 203:87
15. Li HY, Yue YH, Miao CX, Xie ZK, Hua WM, Gao Z (2007) *Catal Commun* 8:1317
16. Michorczyk P, Ogonowski J (2003) *Appl Catal A* 251:425
17. Michorczyk P, Gora-Marek K, Ogonowski J (2006) *Catal Lett* 109:195
18. Saito M, Watanabe S, Takahara I, Inaba M, Murata K (2003) *Catal Lett* 89:213
19. Zheng B, Hua WM, Yue YH, Gao Z (2005) *J Catal* 232:143
20. Xu BJ, Zheng B, Hua WM, Yue YH, Gao Z (2006) *J Catal* 239:470
21. Xu BJ, Li T, Zheng B, Hua WM, Yue YH, Gao Z (2007) *Catal Lett* 119:283
22. Takahashi M, Nakatani T, Iwamoto S, Watanabe T, Inoue M (2006) *Ind Eng Chem Res* 45:3678
23. Takahashi M, Nakatani T, Iwamoto S, Watanabe T, Inoue M (2007) *Appl Catal B* 70:73
24. Arean CO, Delgado MR, Montouillout V, Massiot D (2005) *Z Anorg Allg Chem* 631:2121
25. Takahashi M, Inoue N, Takeguchi T, Iwamoto S, Inoue M, Watanabe T (2006) *J Am Ceram Soc* 89:2158
26. Kasper E, Schuh A, Bauer G, Hollander B, Kibbel H (1995) *J Crystal Growth* 157:68