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Enhanced Stability of HZSM-5 Supported Ga_2O_3 Catalyst in Propane Dehydrogenation by Dealumination

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Abstract Gallium oxide catalysts supported on HZSM-5 with different Si/Al ratios were characterized by pyridine adsorption FT-IR, model reactions and XPS studies. As the Si/Al ratio of the support HZSM-5 zeolite rises, the acidity of the supported catalysts decreases accordingly, which comes from two aspects: the loss of acid sites present on HZSM-5 support and the loss of the acid sites present on gallium oxides. The latter was caused by the change in the interaction between Ga_2O_3 and support. The initial activity in the propane dehydrogenation decreases with increasing Si/Al ratio while the stability increases. The enhanced stability is thought to be caused by the decrease of the acidity of the catalysts, resulting in the suppression of the side reactions, such as cracking and oligomerization.

Keywords Ga_2O_3/HZSM-5 · Propane · Dehydrogenation · Acidity · Stability

1 Introduction

The process of catalytic dehydrogenation of propane into propene is of increasing interest since the production propene from steam cracking and FCC is not sufficient to meet the increasing needs of the market. Dehydrogenation of propane is an endothermic reaction which requires relatively high temperature to obtain high yield of propene. Thermal cracking side reactions are favoured at high temperature, leading to a decrease in product yield and an increase in catalyst deactivation. The oxidative dehydrogenation of alkanes by carbon dioxide has been proposed as an alternative. Rather high selectivity towards propene has been reported over some catalysts, such as rare earth vanadates [1], supported Cr_2O_3 [2], and Ga_2O_3 [3, 4]. And it has been found that carbon dioxide can markedly promote the dehydrogenation of ethane and propane over gallium oxide catalysts [5]. However, no agreement on the main role of carbon dioxide in reaction has been reached yet. Nakagawa et al. proposed CO_2 promoted desorption of olefin products from the catalyst surface [6], and Michorzyk et al. considered CO_2 consumed hydrogen via reverse water gas shift reaction [4]. In our previous work it was found that the reverse water gas shift reaction and the Boudouard reaction of CO_2 may account for the enhanced catalytic activity and stability over Ga_2O_3 catalysts [3]. Besides, the stability of these catalysts is still rather poor and the activity declined dramatically with the reaction time, which is fatal for industrial application [1–4].

Aromatization of light paraffins over Ga-promoted HZSM-5 catalysts has been studied intensely in the previous decade. The role of gallium in the aromatization reaction has been investigated by numerous experimental [7–13] and theoretical [14–21] studies. Many authors agree that the aromatization reaction occurs via a bifunctional mechanism, and gallium enhances the dehydrogenation steps including the dehydrogenation of alkane, higher olefins and cycloolefins [7–13]. More recently, dehydrogenation of propane to propene in the presence of CO_2 was investigated over gallium oxide catalysts supported on HZSM-5 with different Si/Al ratios [22]. It was found that the catalytic behavior was greatly influenced by the Si/Al ratio of HZSM-5 support. With increasing Si/Al ratio, the initial activity of HZSM-5 supported Ga_2O_3 catalysts decreases while the catalytic stability increases. A highly

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active and stable catalyst was obtained, with a propene yield of about 22% without any observable trend of deactivation in 100 h. In this study, gallium oxide catalysts supported on HZSM-5 with different Si/Al ratios were characterized by pyridine adsorption FT-IR, model reaction and XPS studies. The possible reasons for the different catalytic behaviors as well as the enhanced stability in the reaction through dealumination were discussed.

2 Experimental

2.1 Catalyst Preparation

HZSM-5 zeolite with a Si/Al ratio of 60 was supplied by Shanghai Research Institute of Petrochemical Technology. HZSM-5 with different Si/Al ratios were prepared by dealumination of HZSM-5 with a Si/Al ratio of 60 at various steaming temperatures (600, 650, 700, 750 and 800 °C) for 6 h, followed by washing with 1 mol/L HNO_3 at 95 °C for 24 h, filtering, drying and calcining at 600 °C for 6 h. DRS results confirm that the higher the steaming temperature is, the higher the Si/Al ratio of the treated HZSM-5 is [22, 23]. Since the results of chemical analysis of HZSM-5 with high Si/Al ratios are often ambiguous, the steaming temperature is used in the text to stand for the difference of Si/Al ratio.

Supported gallium oxide catalysts were prepared by impregnating an aqueous solution containing a calculated amount of $Ga(NO_3)_3 \cdot xH_2O$ (Aldrich) on HZSM-5 with different Si/Al ratio or silicalite using an incipient wetness method. The impregnated samples were dried at 100 °C and calcined at 600 °C for 6 h in air flow. The obtained catalysts were designated as Ga_2O_3/HZSM-5(x) and Ga_2O_3/silicalite, respectively, in which x represents the steaming temperature of the HZSM-5 support. Ga_2O_3/HZSM-5 stands for non-steam treated HZSM-5 supported gallium oxide catalyst. The weight percentage of Ga_2O_3 in all catalysts was 5%. XRD results indicate that gallium oxide is well dispersed on all the supports since no other diffraction peaks except those of the HZSM-5 supports were observed.

β-Ga_2O_3 was obtained by directly calcining $Ga(NO_3)_3$ xH_2O (Aldrich) at 600 °C for 6 h in air flow.

2.2 Catalyst Characterization

FT-IR spectra of pyridine adsorption were recorded on a Nicolet Nexus 470 FT-IR spectrometer furnished with an in situ sample cell. A self-supporting disk of the sample (ca. 11 mg) was pretreated at 300 °C for 4 h under a vacuum of 10^{-2} Pa and then cooled to room temperature. FT-IR spectra were recorded after the pyridine adsorption at room temperature for 30 min and evacuation at a desired temperature for 30 min. The X-ray photoelectron spectra (XPS) were obtained by using Al-Kα radiation (1,486.6 eV) on a Perkin-Elmer PHI 5000C ESAC system with a base pressure of 1×10^{-9} Torr. The sample was pressed and degassed in the pretreatment chamber for 2 h before being transferred to the analysis chamber for XPS measurement. All binding energy (BE) values were referenced to the C1s peak at 284.6 eV.

2.3 Reaction Testing

The activities of the samples toward cumene cracking were tested in a pulse microreactor. The catalyst (10 mg) was preheated at 450 °C for 2 h before reaction. Hydrogen with a flow rate of 60 mL/min was used as the carrier gas. The reaction was conducted at 250 °C, and 1 μL cumene was injected for each test. The products were analyzed by an on-line gas chromatograph equipped with a TCD.

Catalytic tests for propane dehydrogenation were performed at 600 °C in a fixed-bed flow microreactor at atmospheric pressure. The catalyst load was 200 mg, and it was activated at 600 °C for 1 h in nitrogen flow prior to the reaction. Typically, the gas reactant contained 2.5 vol% propane, 5 vol% carbon dioxide and balancing nitrogen. The total flow rate of feed gas was 20 mL/min.

The hydrocarbon reaction products were analyzed using an on-line gas chromatograph equipped with a 6-m packed column of Porapak Q and a FID. The gas products, such as N_2, CO and CO_2, were analyzed on-line by another chromatograph equipped with a 2-m packed column of carbon molecular sieve 601 and a TCD. The conversion and selectivity were calculated as follows:

$$C_3H_8\text{conversion} = \frac{C_3H_{8\ \text{in}} - C_3H_{8\ \text{out}}}{C_3H_{8\ \text{in}}} \times 100\%,$$

$$CO_2\text{conversion} = \frac{CO_{2\ \text{in}} - CO_{2\ \text{out}}}{CO_{2\ \text{in}}} \times 100\%,$$

$$C_3H_6\text{yield} = \frac{C_3H_{6\ \text{out}}}{C_3H_{8\ \text{in}}} \times 100\% .$$

3 Results

3.1 Acidity Measurement

The acid sites on HZSM-5 supported gallium oxide catalysts was investigated by pyridine adsorption IR method, and the FT-IR spectra is shown in Fig. 1. Both Brønsted (1,540 cm^{-1}) and Lewis (1,450 cm^{-1}) acid sites are

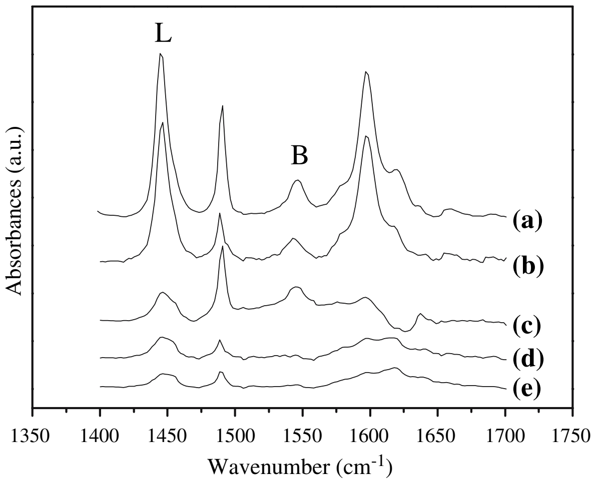

Fig. 1 FT-IR spectra of supported gallium oxide catalysts after adsorption of pyridine and desorption at 100 °C: (**a**) Ga_2O_3/HZSM-5;(**b**) Ga_2O_3/HZSM-5(600);(**c**) Ga_2O_3/HZSM-5(700);(**d**) Ga_2O_3/HZSM-5(750);(**e**) Ga_2O_3/HZSM-5(800)

observed on the catalysts. Brønsted and Lewis acidities are quantified into integrated areas of the absorbances at 1,540 and at 1,450 cm^{-1}, respectively, and the results are summarized in Fig. 2 and 3. It can be seen that most Lewis acid sites are of weak acid strength, while most Brønsted acid sites are of medium to strong strength. The acid sites on gallium oxide are believed to be Lewis acid sites [24] and the acid sites on HZSM-5 are thought to be Brønsted ones, since the amount of the Lewis acid sites on HZSM-5 is only 7% as that on Ga_2O_3/HZSM-5. When the Si/Al ratio of the ZSM-5 support is increased, the amount of both Brønsted and Lewis acid sites decreases, which is in agreement with NH_3-TPD results reported in our previous studies [22]. The decreasing trend is more obvious for Bronsted acid sites. This is quite comprehensible since the presence of the Brønsted acid sites on HZSM-5 supported gallium oxide catalysts should be directly related to the framework Al species, which would be reduced after dealumination. It is interesting to note that the Lewis acid sites are also decreased by dealumination. This decrease should be attributed to the loss of acid sites present on gallium oxides, which has been proved by NH_3-TPD results, since the amount of acid sites reduced by dealumination is greater than that of total acid sites which HZSM-5 originally possesses. Our previous studies show that strong interaction between Ga_2O_3 species and the support enhanced the acid strength of the supported gallium oxides [25]. So, the above decrease in Lewis acid amount may be connected with the change in the interaction between Ga_2O_3 species and the HZSM-5 support.

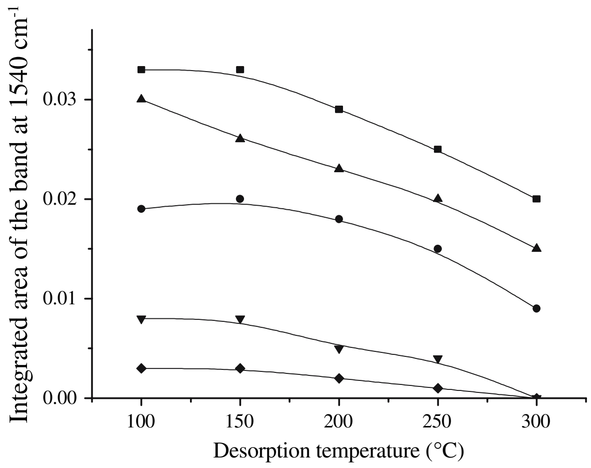

Fig. 2 Amount of Brønsted acidity at different desorption temperatures: ■ Ga_2O_3/HZSM-5; ▲ Ga_2O_3/HZSM-5(600); ● Ga_2O_3/HZSM-5(700); ▼ Ga_2O_3/HZSM-5(750); ◆ Ga_2O_3/HZSM-5(800)

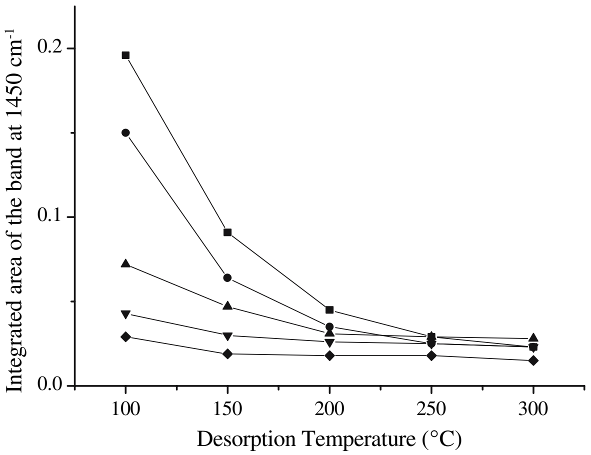

Fig. 3 Amount of Lewis acidity at different desorption temperatures: ■ Ga_2O_3/HZSM-5; ● Ga_2O_3/HZSM-5(600); ▲ Ga_2O_3/HZSM-5(700); ▼ Ga_2O_3/HZSM-5(750); ◆ Ga_2O_3/HZSM-5(800)

The catalytic activities of different supported gallium oxide catalysts toward cumene cracking, a typical strong acid catalyzed reaction, have been investigated. The results are given in Table 1. The activity of the supported gallium oxide catalysts decreases with the increase of the Si/Al ratio of HZSM-5 support, which is in agreement with NH_3-TPD and pyridine adsorption IR results. This shows that the change in Si/Al ratio of the support has certain impact on the interaction, resulting in the reduced amount of strong acid sites. This is in accordance with the above explanation is that the strong interaction between HZSM-5 and Ga_2O_3 could generate new strong acid sites.

The acidity of the deactivated catalysts is also measured using cumene cracking as a model reaction, and the results are listed in Table 1 as well. It can be seen that the activity decreases severely after propane dehydrogenation reaction for 24 h for all supported gallium oxide catalysts, indicating that part of strong acid sites were poisoned by coke during dehydrogenation process. The decreasing percent of the activity reduces with the increase of the Si/Al ratio of

Table 1 Catalytic activities for cumene cracking at 250 °C

Catalyst	Cumene conversion (%)		Decrease (%)
	Fresh	Used[a]	
HZSM-5	7.2	–	–
HZSM-5(600)	6.1	–	–
HZSM-5(700)	4.7	–	–
HZSM-5(800)	2.7	–	–
β-Ga_2O_3	0.5	–	–
Ga_2O_3/HZSM-5	28	3.5	88
Ga_2O_3/HZSM-5(600)	23	4.5	80
Ga_2O_3/HZSM-5(650)	22	6.3	71
Ga_2O_3/HZSM-5(700)	20	11	45
Ga_2O_3/HZSM-5(750)	12	8.0	33
Ga_2O_3/HZSM-5(800)	2.7	2.0	26

[a] after propane dehydrogenation reaction for 24 h

HZSM-5 support, which is in line with the catalyst stability during the dehydrogenation. This indicates that strong acid sites poisoned by coke may account for the deactivation during the dehydrogenation. Ga_2O_3/HZSM-5(700) catalyst, which has the highest cumene cracking activity after deactivation, also shows the highest steady state dehydrogenation activity.

3.2 XPS Studies

In order to elucidate the interaction between Ga_2O_3 and the HZSM-5 support, the XPS spectra of the supported gallium oxide catalysts were recorded, and the results are listed in Table 2. The Ga 3d binding energy is increased after gallium oxide is supported on HZSM-5 with a Si/Al ratio of 60 (21.3 eV), as compared with that in β-Ga_2O_3 (20.8 eV), which shows that a strong interaction exists between the Ga_2O_3 species and the HZSM-5 support. It could be noted that the Ga 3d binding energy in Ga_2O_3/HZSM-5 is similar to that in Ga_2O_3/γ-Al_2O_3 (21.5 eV), indicating the interaction between Ga_2O_3 and support is similar in Ga_2O_3/HZSM-5 and Ga_2O_3/γ-Al_2O_3. One possible reason for this resemblance is that Ga_2O_3 species interact preferentially with framework Al species in HZSM-5. In the previous literature, the interaction between protonic sites of mordenite zeolite and extra-framework oxoaluminium deposits in the zeolite voids was observed, which could generate new strong acid sites [26]. Since gallium, which is in the same family as aluminum in periodic table, has very similar chemical property with aluminum, so the interaction between gallium oxide species and framework aluminum resembles that between aluminum oxide species and protonic sites of zeolites. Of course, this deserves further studies. The Ga 3d binding energy of the HZSM-5 supported gallium oxide decreases with increasing Si/Al ratio, and gradually approaches that of Ga_2O_3/SiO_2 (20.3 eV), indicating that the interaction between Ga_2O_3 species and framework Al species weakens as the Al content reduces due to the dealumination of the support. The interaction has become the one between Ga_2O_3 species and Si species in the support at that time.

Table 2 XPS data of supported gallium oxide catalysts

Catalyst	Steaming temperature (°C)	Ga 3d binding energy (eV)
β-Ga_2O_3	–	20.8 [3]
Ga_2O_3/γ-Al_2O_3	–	21.5 [25]
Ga_2O_3/HZSM-5	–	21.3
Ga_2O_3/HZSM-5(600)	600	21.1
Ga_2O_3/HZSM-5(650)	650	21.0
Ga_2O_3/HZSM-5(700)	700	20.9
Ga_2O_3/HZSM-5(750)	750	20.6
Ga_2O_3/HZSM-5(800)	800	20.5
Ga_2O_3/Silicalite	–	20.3
Ga_2O_3/SiO_2	–	20.3 [25]

4 Discussion

The dehydrogenation of propane over gallium oxide or supported gallium oxide catalysts in the presence of CO_2 has been suggested to proceed through a heterolytic dissociation reaction pathway on the Ga_2O_3 surface [27]. When both Ga_2O_3 and H^+ are present on the catalyst, the conjugated effect of gallium oxide and proton is to replace the slow limiting step by the fast equilibrium.

This reaction mechanism gives a good explanation for the decrease of the initial propane dehydrogenation activity over HZSM-5 supported gallium oxide catalysts with increasing Si/Al ratio of the support, as shown in Fig. 4 [22]. NH_3-TPD and pyridine adsorption FT-IR results show that the amount of medium to strong acid sites reduces substantially as the Si/Al ratio of the HZSM-5 support increases. This trend is especially phenomenal for Brønsted acidities measured by pyridine adsorption FT-IR method. The lack of acid sites with medium to strong strength would inhibit the heterolytic dissociated adsorption of propane on the Ga_2O_3 surface as well as the exchange reaction between the propyl carbenium ion and a proton, leading to a reduction in activity for propane dehydrogenation. This reduction in the initial dehydrogenation activity correlates very well with the decrease in the activity of cumene cracking as shown in Fig. 5. The decrease in the acidity of supported gallium oxide catalysts upon dealumination of support may come from two factors:

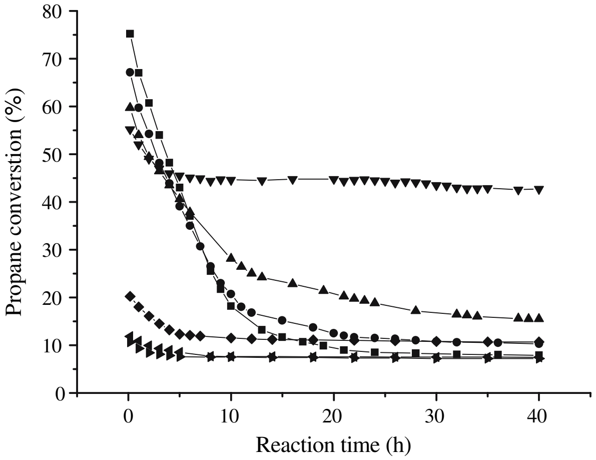

Fig. 4 Propane conversion of the catalysts as a function of reaction time [6]: ■ Ga_2O_3/HZSM-5; ● Ga_2O_3/HZSM-5(600); ▲ Ga_2O_3/HZSM-5(650); ▼ Ga_2O_3/HZSM-5(700); ◆ Ga_2O_3/HZSM-5(750); ◀ Ga_2O_3/HZSM-5(800); ▶ Ga_2O_3/silicalite

the loss of acid sites present on HZSM-5 support and the altered interaction between Ga_2O_3 and support caused by the change in the composite of HZSM-5 support. The latter seems to make the major contribution since according to NH_3-TPD results [22], the amount of acid sites reduced is greater than that of total acid sites which HZSM-5 originally possesses. Therefore, the interaction between Ga_2O_3 and support plays a vital role in determining the surface acidity of the supported catalysts, which is further verified by the model strong acid catalyzed reaction.

XPS results verify the existence of the interaction between the gallium oxide and the HZSM-5 support, since increased Ga 3d binding energy was observed in Ga_2O_3/HZSM-5 as compared with that in β-Ga_2O_3. As the amount of framework Al species in HZSM-5 support reduces by dealumination, Ga 3d binding energy declines, indicating that these interactions weaken. It is reported that the acidity of the supported gallium oxide catalysts would be enhanced by the strong interaction between supported Ga_2O_3 species and the support [28]. Therefore, the decrease in acidity of supported gallium oxide catalysts with increasing the Si/Al ratio of HZSM-5 support could be attributed to the fact that there is less framework Al species with which gallium oxide can interact to produce medium to strong acid sites. Similar results were observed in our previous work showing that strong acidity of Ga_2O_3/γ-Al_2O_3 comes from the strong interaction between Ga_2O_3 and γ-Al_2O_3 support, while weak acidity of Ga_2O_3/SiO_2 is due to weak interaction between Ga_2O_3 and SiO_2 support [25].

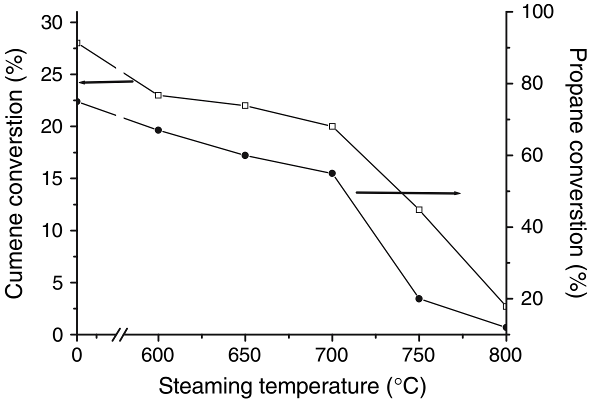

Fig. 5 Correlation between the cumene conversion (□) and the propane conversion (●) over fresh HZSM-5 supported gallium oxide catalysts with different steaming temperatures

Meanwhile, the major side reactions during the propane dehydrogenation, such as oligomerization, cyclization and cracking, would also occur on the acid sites [29]. Coke is formed via these side reactions. It is well believed that catalyst deactivation in dehydrogenation reactions is generally attributed to the coke deposition on the catalyst surface. Thus, inhibiting these side reactions through decreasing the acid site concentration on the catalysts would improve the stability of the catalysts for propane dehydrogenation, which can be achieved by decreasing the amount of acid sites on HZSM-5 and weakening the interaction between Ga_2O_3 species and Al species in HZSM-5 support though dealumination. This is the reason why the stability of supported Ga_2O_3 catalysts is significantly enhanced by dealumination. The cumene cracking activity drops 88% for used Ga_2O_3/HZSM-5 catalyst (after 24 h in propane dehydrogenation) compared with fresh catalyst, while in the case of Ga_2O_3/HZSM-5(700) and Ga_2O_3/HZSM-5(800), the cumene cracking activity falls only 45% and 26%, respectively. Correspondingly, the propane conversion over Ga_2O_3/HZSM-5 has a net decrease of 65% and in contrast, in the case of Ga_2O_3/HZSM-5(700), only a net decrease of 12% is observed [22]. Therefore, the steady state activity of dehydrogenation is determined not only by the initial activity but also by the stability of the catalysts. The steady state activity of the catalysts exhibits a volcano shaped curve versus the Si/Al ratio of the supports, as illustrated in Fig. 6, which correlates very well with the change of the activities of the deactivated catalysts in cumene cracking.

Therefore, it could be concluded that the presence of strong acid sites on supported gallium oxide catalysts has two contrary roles in the propane dehydrogenation reaction. The positive role is to enhance the catalyst activity by providing alternative reaction path to the slow step. The negative role is to accelerate the catalyst deactivation by catalyzing a series of side reactions. The amount of strong acid sites present on supported gallium oxide catalysts should strike a balance between these two contrary aspects, which can be realized through dealumination of HZSM-5 support. This goal is achieved in the case of Ga_2O_3/HZSM-5(700), which is active and highly stable for propane dehydrogenation.

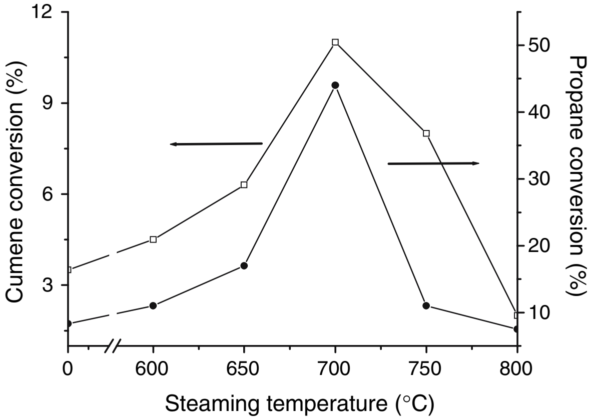

Fig. 6 Correlation between the cumene conversion (□) and the propane conversion (●) over deactivated HZSM-5 supported gallium oxide catalysts with different steaming temperatures

5 Conclusions

The stabilities of HZSM-5 supported gallium oxide catalysts in the propane dehydrogenation can be enhanced by dealumination of HZSM-5 support. This enhancement was attributed to the decreasing of the amount of acid site with medium to strong strength on the catalysts, resulting in the decreasing of coke formation via side reactions such as oligomerization, cyclization and cracking. The acid sites reduction by dealumination come not only from the decreasing the acid sites on HZSM-5 supported directly related to the framework Al species, but also from the decreasing the acid sites on gallium oxide caused by weakening the interaction between the gallia and support. Meanwhile, strong acid sites can enhance the activity by replacing the rate limiting step by two fast equilibriums. The amount of strong acid sites present on supported gallium oxide catalysts should strike a balance between these two contrary aspects.

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