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ARTICLE TYPE

Mechanistic insight to effect of acidity of Ga/HZSM-5 on its activity for propane aromatization**He Xiao,^{a,b} Junfeng Zhang,^a Peng Wang,^{a,b} Zhenzhou Zhang,^{a,b} Qingde Zhang,^a Hongjuan Xie,^a Guohui Yang,^a Yizhuo Han^a and Yisheng Tan^{a,*}**

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Ga-modified HZSM-5 precursors, containing 1wt% Ga, were firstly prepared using incipient wetness impregnation method, and then subjected to one or three-time consecutive treatment by cycles of reduction in hydrogen and re-oxidation in air. The resulting Ga/HZSM-5 catalysts were characterized by N₂ physical adsorption, ICP-AES, DRIFT, Py-FTIR, NH₃-TPD, H₂-TPR, XPS, DRIFT-TPSR and MS-TPSR techniques in order to clear mechanistic details that the acidity of these Ga/HZSM-5 catalysts affected their activity for propane aromatization. The characterization data suggested that the impregnated introduction of Ga to ZSM-5 zeolite and subsequent reduction-oxidation treatment led to a great decline in the numbers of Brønsted acid sites (BAS) and promoted the formation of strong Lewis acid sites (LAS) attributed to highly dispersed Ga species facilely. The formed strong LAS were special for promoting the dehydrogenation steps during propane aromatization, while the original BAS were responsible for the whole aromatization processes. The TPSR results suggested that propane was converted to propylene through the dehydrogenation on BAS and strong LAS, and simultaneously converted to ethylene through the β-scission on BAS at low temperature. With the elevation of temperature, the generated propylene and ethylene on the strong BAS and the strong LAS were further converted into BTX aromatics accompanied by hydrogen release. It was plausible that the highly efficient synergy between BAS and strong LAS could result in lower aromatization temperature and more product of benzene (β state) over the Ga/HZSM-5 catalysts than that over the Ga-modified HZSM-5 precursors.

1. Introduction

The worldwide supply of liquefied petroleum gas (LPG) was about 140 million metric tonnes in 1990 and rose to about 275 million metric tonnes by year 2014.¹ Meanwhile, urgent demand of BTX (benzene, toluene and xylene) has drawn academic and industrial sectors' attention to deeply investigate the conversion of lower alkanes into these aromatics. Therefore, propane (light alkane) aromatization has been extensively studied in recent years. Previous researches²⁻¹⁷ focused on the bifunctional Ga modified ZSM-5 catalysts for aromatization because of their superior catalytic performance to Zn and Pt modified ZSM-5 catalysts.^{4, 8} It was found that incorporation of Ga to ZSM-5, which prepared using different preparation methods such as hydrothermal *in-situ* synthesis and post synthesis treatment (ion-exchange, impregnation, chemical vapour deposition [CVD] and reduction-oxidation treatment), could adjust the acidity of Ga/ZSM-5 catalysts. And the varied acidity in turn had a significant effect on the propane aromatization performance of the catalysts.^{4, 6} Choudhary *et al.*¹⁸ found that the Si/Ga and Si/Al ratios of H-gallosilicate (MFI) prepared using *in-situ* hydrothermal synthesis method strongly affected its acidity/acid strength distribution, thereby inducing a dramatical difference of catalytic activity/selectivity in propane aromatization. The

highest propane conversion and selectivity of aromatics over these HMF1 catalysts could come to about 75% and 80% respectively. Besides, Al-Yassir *et al.*¹⁶ further reported that, through degallation from the ZSM-5 framework in hydrothermal synthesis process, Lewis acid sites (LAS) associated with highly dispersed and reducible extra-framework Ga₂O₃ were generated on catalyst surface, which finally resulted in high activity of propane aromatization. The optimal propane conversion and selectivity of BTX achieved to 42.0% and 52.0 % respectively. El-Malki *et al.*¹⁹ prepared a highly efficient Ga/ZSM-5 catalyst for aromatization using a CVD method together with subsequent water treatment. They found that the subsequent treatment with water to the catalyst could create secondary strong Brønsted acid sites (BAS), contributing to the aromatization activity of Ga/ZSM-5 catalyst. Abdul Hamid *et al.*²⁰ revealed that the reductive atmosphere could promote the migration of Ga species and formation of active Ga species, which further affected the acidity of Ga/HZSM-5 catalysts. These active Ga species and BAS over ZSM-5 had a synergetic effect on the catalytic performance of the Ga/HZSM-5 catalysts. The highest propane conversion and selectivity of BTX were not more than 10 % and 40% respectively. Nowak *et al.*³ investigated the effect of H₂-O₂ cycles on the activity of Ga/HZSM-5 prepared using ion-exchange method. They found the synergistic effect between the

reduced state Ga species generated by H₂-O₂ treatment and BAS over the ZSM-5 zeolites contributed to the highest selectivity of aromatics, which got to 19.1% at high conversion (97–99%) for the aromatization of propane at 823 K using Ga/(0.5) as catalysts.

Through the structure-activity correlations between the acidity of Ga/ZSM-5 catalyst and its activity, Rodrigues *et al.*^{3, 10, 11, 20} thought that the reduction-oxidation treatment promoted the formation of highly dispersed oxidic gallium species which were anchored to ion-exchange sites of the zeolite framework, and contributed to the strong LAS. Meanwhile, it was also found that the synergy between LAS and BAS led to alkane aromatization activity rather than exclusive effect of LAS or BAS in the reaction. It was believed that the reducibility of strong Lewis acid species facilitated the formation of reduced gallium species that was the actual active site in alkane activation. As observed, initial rates of propane conversion were at least 20 times higher for their obtained Ga-containing catalysts than the respective zeolite but were almost independent of gallium content. Considering the aromatization activities alone, gallium impregnation led to catalysts approximately 200 times more active in the case of the TZ35 series because of synergy between LAS and BAS.

In our previous work,¹³ a highly efficient Ga/ZSM-5 catalyst was prepared by formic acid impregnation and *in-situ* treatment for propane aromatization. This novel treatment process promoted the formation of strong LAS attributed to highly dispersed (GaO)⁺ species through decomposition of intermediate species and the interaction between Ga₂O₃ and water steam. Based on the investigation of the catalytic system, it was thought that the high catalytic activity of this catalyst was attributed to the synergistic effect between strong LAS and the BAS. The highest propane conversion and selectivity of BTX on the Ga/HZSM-5 catalyst we prepared by this novel method were 53.6% and 58.0% respectively. It's obvious that the activities of the catalysts prepared using different methods are different. Considering the distinction of test conditions, it is reluctant to make a certain conclusion that which preparation method is more preferential to obtain good catalytic performance. But it is widely acknowledged that the presence of highly dispersed Ga on HZSM-5, which is obtained through special treatment process such as reduction-oxidation operation, is favorable for propane aromatization. This is evidenced from our present work. In present work, the preparation process of the Ga/HZSM-5 and the formation process of active Ga species are different from the previous work.¹³ Ga-modified HZSM-5 precursors were firstly prepared using incipient wetness impregnation method, and then subjected to one or three-time consecutive treatment by cycles of reduction in hydrogen and re-oxidation in air. The reduction-oxidation treatment could promote the migration of these Ga species into the zeolite and formation of highly dispersed (GaO)⁺ species inferred from our techniques and previous research.^{3, 11} It was apparent that both these two different preparation processes (previous treatment and present treatment) promoted the formation of (GaO)⁺ species. Wherein, propane conversion and selectivity of the Ga/HZSM-5 catalyst prepared using reduction-oxidation method showed a significant increase of 15.2% ~ 22.3% and 9.5% ~ 10.9% respectively in contrast to that of the Ga/HZSM-5 catalyst prepared using traditional impregnation method at the same test conditions. The superior activity of

Ga/HZSM-5 catalyst prepared using reduction-oxidation method was attributed to the synergistic effect between the strong LAS generated by the (GaO)⁺ species and the BAS. Conclusively, it's apparent that the reduction-oxidation treatment improves the activity of Ga containing HZSM-5 zeolites greatly. Simultaneously, it's obvious that, if one looks forward to a high activity of Ga/ZSM-5 catalyst for propane aromatization, obtaining a suitable amount of BAS and LAS related to Ga species through adopting some various/special preparation and treatment methods is necessary.

The previous work focused on a novel proposal preparation method for catalyst and the probable formation route of highly active GaO⁺ species.¹³ While, in present work, we concentrated on the systematical investigation that how acidity of Ga/HZSM-5 catalyst affected the evolution of reactants and intermediates (such as β -scission of propane to methane and ethylene and dehydrogenation of propane to propylene) on specific acid sites (BAS and LAS) of Ga/HZSM-5 as well as the sorption/desorption process of reactants and intermediates on these acid sites. In other words, we paid more attention to the relationship between the acid sites (LAS and BAS) and specific reactions as well as the sorption/desorption of reactants and intermediates, as the systematical investigation on this research was not reported to our knowledge. Therefore, in this paper, we in-detail rationalized the results in terms of correlations between the acidity (Lewis acidity and Brønsted acidity) of Ga/HZSM-5 catalyst and its reactivity (specific reactions as well as the sorption/desorption process of reactants and intermediates) in propane aromatization by various characterizations of the catalysts such as N₂ physical adsorption, ICP-AES, DRIFT, Py-FTIR, NH₃-TPD, H₂-TPR, XPS, DRIFT-TPSR and MS-TPSR techniques. And the mechanistic details that the acidity of the Ga/HZSM-5 catalysts affected their activity for propane aromatization were illustrated deeply.

2. Experimental section

2.1 Catalyst preparation

HZSM-5 zeolites (silica to aluminum mole ratio = 19) were bought from Nankai University. Ga was incorporated into this zeolite by incipient wetness impregnation with gallium nitrate solution (1wt% Ga loading). The impregnated sample was calcined at 550 °C for 5 h under static air. Thus, the Ga/IM catalyst was gained accordingly. Afterward, 0.15 g of Ga/IM catalyst was placed in a micro fixed-bed reactor and then subjected to the reduction-oxidation treatment. Here, reduction was performed under a hydrogen flow of 15 mL/min at 540 °C for 1 h and re-oxidation under an air flow of 15 mL/min for 1 h. The resulting catalysts were denoted as Ga/IMRO1C and Ga/IMRO3C respectively based on one and three times reduction-oxidation treatment to Ga/IM.

2.2 Catalyst characterization

The textural properties of catalyst were measured by N₂ physical sorption at 77K using a Tristar 3000 machine. Surface areas were calculated by the BET method and micro-, meso-, and macropore volumes were calculated by the t-plot method.

The powder X-ray diffraction (XRD) patterns were measured on a Rigaku MiniFlex II X-ray diffractometer using CuK α

radiation. The anode was operated at 40 kV and 40 mA. The 2θ angles were scanned from 5° to 60°.

TEM micrographs were obtained by a JEOL-JEM-2100F transmission electron microscope operating at 200 kV.

Diffuse reflectance infrared spectra (DRIFT) measurements were performed using a Bruker Tensor 27 instrument with a MCT detector (64 scans, 4 cm⁻¹). Weight 20 mg of catalyst and put it in an infrared cell with KBr windows for *in-situ* treatments. The DRIFT spectra were recorded after treating the catalyst at 300 °C for 1 h with a flow of argon.

Pyridine-adsorbed Fourier Transform Infrared Spectroscopy (Py-FTIR) was used to determine the amount of BAS and LAS using Bruker Tensor 27 equipment. 20 mg of catalyst was pressed into a regular wafer (R = 1.3 cm⁻¹) and put in an infrared cell. The determination of the infrared spectrum was made after sample treatment at 400 °C for 2 h under vacuum, and this spectrum was used as background for the adsorbed pyridine experiments. Pyridine was then adsorbed to a 5.0 × 10⁻² Pa equilibrium pressure at 40 °C. FTIR spectra were recorded after consecutive evacuation at 150, 250, 350 and 450 °C.

The temperature-programmed desorption of ammonia (NH₃-TPD) was used to test the amount and strength of the acid sites of as-prepared catalysts in TP-5080 chemisorption instrument. The catalyst (100 mg) was pre-treated at 500 °C under a flow of N₂ (30 ml/min) for 2 h and then cooled down to 100 °C. Then NH₃ was introduced into the flow system. The TPD spectra were recorded at a ramp rate of 10 °C/min from 100 °C to 700 °C.

The H₂-Temperature-programmed reduction (H₂-TPR) was carried out to study reducibility of the catalysts with chemisorption instrument (TP-5080). The catalyst (100 mg) was pre-treated at 500 °C under a flow of N₂ (32 ml/min) for 1 h and then cooled down to 100 °C, then changed to H₂/N₂ = 0.09 mixture (35 ml/min). The temperature-programmed reduction was performed between 100 °C and 900 °C with a ramp rate of 10 °C/min.

X-ray photoelectron spectroscopy (XPS) was used to analyze the change of surface composition measured by AXIS ULTRA DLD equipment. The following photoelectron lines were recorded: Ga2p_{3/2}, Ga2p_{1/2}, Ga3d, Si2p, Al2p, O1s, O2s and C1s. The binding energy values were corrected for charging effect by referring to the adventitious C1s line at 284.5 eV.

Diffuse reflectance infrared spectra (DRIFTS) investigation of temperature-programmed surface reaction (TPSR) was carried out in an *in-situ* reaction cell. The catalyst (20mg) was pre-treated at 400 °C under a flow of argon (30 ml/min) for 1 h and then cooled down to 50 °C. After that, propane flow was introduced to the reaction cell for absorption for 0.5 h and then switched to the argon flow (30 ml/min) to remove the physical adsorption of propane (blowing for 0.5 h). The above-treated sample was heated from 50 °C to 450 °C at a ramp rate of 3 °C/min, meanwhile its diffuse reflectance infrared spectra were recorded.

Mass spectrum investigation of temperature programmed surface reaction (MS-TPSR) was carried out on chemisorption instrument (TP-5080) and OMNI star. The catalyst (100 mg) was firstly pre-treated at 500 °C for 1 h under a flow of argon (30 ml/min) and then cooled down to 50 °C. After that, propane was introduced into the flow system until saturation sorption (about 0.5 h). The sample was heated again from 50 °C to 650 °C with a

ramp rate of 3 °C/min and the effluents from the reactor were analysed by an on-line mass spectrometer synchronously.

2.3 Catalyst evaluation

The catalyst test, as our previous illustration,¹³ was carried out in a horizontal quartz tube fixed-bed reactor at T = 540 °C, P = 100 kPa, WHSV = 6000 ml/(g·h) and with a N₂/C₃H₈ molar ratio of 2. Outlet gas was analysed after 0.5-4.5 h reaction.

The products were analysed by online gas chromatograph (HUAAI GC 9560) equipped with a flame ionization detector (FID) with HP-INNOWAX capillary column, off-line gas chromatograph (HUAAI GC 9560) equipped with a FID with Al₂O₃ packed column, and offline gas chromatograph (East & West GC 4000A) equipped with a thermal conductivity detector (TCD) with carbon molecular sieves packed column, respectively. The propane conversion and product selectivity were calculated using the following eqn (1) and (2).

$$X_{propane} = \frac{(N_{propane,in} - N_{propane,out})}{N_{propane,in}} \times 100\% \quad (1)$$

$$S_i = \frac{N_{i,out}}{\sum N_{i,out}} \times 100\% \quad (2)$$

where $X_{propane}$ is the conversion of propane, S_i is the selectivity of target product i ($i = \text{BTX}, \text{CH}_4, \text{etc}$), $N_{propane,in}$ and $N_{propane,out}$ are the numbers of moles of propane in the inlet and outlet gas phases, respectively, and $N_{i,out}$ is the total number of moles of product i .

3. Results and discussion

3.1 Catalyst composition and textural properties

Table 1 Physical parameters of different catalysts

Sample	S ^a _{BET} (m ² /g)	S ^a _{micro} (m ² /g)	S _{ext} (m ² /g)	V ^b _{total} (m ³ /g)	V ^b _{micro} (m ³ /g)	V _{ext} (m ³ /g)
HZSM-5	420	324	95.8	0.185	0.129	0.056
Ga/IM	400	301	99.1	0.180	0.121	0.059
Ga/IMRO1C	384	275	109	0.177	0.111	0.066
Ga/IMRO3C	381	270	111	0.177	0.109	0.068

^a determined by t-method; ^b determined by Volume adsorbed at p/p⁰=0.97.

Table 2 Bulk and surface compositions of as-prepared catalysts

Sample	Si/Al ratio		Si/Ga ratio	
	Bulk ^a	Surface ^b	Bulk ^a	Surface ^b
HZSM-5	19.1	20.9	/	/
Ga/IM	18.9	17.2	150	21.2
Ga/IMRO1C	19.0	15.1	151	98.0
Ga/IMRO3C	19.0	12.6	151	137

^a determined by ICP-AES method; ^b determined by XPS.

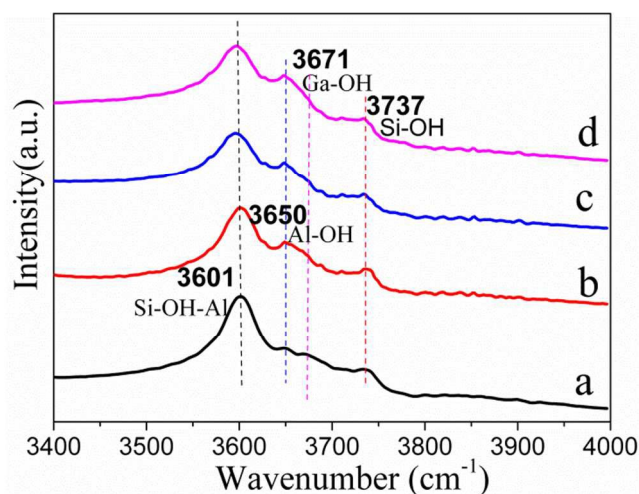


Fig. 1 DRIFT spectra in the OH stretching region of as-prepared catalysts. (a) HZSM-5; (b) Ga/IM; (c) Ga/IMRO1C; (d) Ga/IMRO3C.

The pore volume and BET surface areas (S_{BET}) of different catalysts are obtained based on sorption isotherms of N_2 condensation at 77 K and the results are listed in Table 1. As observed, the micropore surface area and micropore volume of the Ga-containing ZSM-5 zeolites decreases compared to that of HZSM-5, especially for Ga/IMRO1C and Ga/IMRO3C treated by reduction-oxidation process, the decrease is more severe. It is thought that the decrease of micropore surface area and micropore volume is probably due to the pore blockage resulted from the deposition of extra-framework gallium and aluminum species within the micropores.^{11, 13} In addition, compared with surface areas and porous volumes of meso- and macropores of Ga/IM, those of Ga/IMRO1C and Ga/IMRO3C show a slight increase. This indicates that the reduction-oxidation treatment has a potential effect on expansion of the micropores somewhat. TEM characterization of these catalysts is also used to visualize the pore structure. As shown in Fig. S1a, 1b, 1c and 1d, Ga/IMRO1C and Ga/IMRO3C show regular hexagonal prisms like Ga/IM and HZSM-5. It suggests that impregnation and reduction-oxidation treatment slightly affect the morphologies of ZSM-5 zeolites. At the same time, it's found that no irregular pore structures as well as mussy species are created after impregnation and reduction-oxidation treatment, as observed in Fig. S1A, 1B, 1C and 1D. In combination of BET data, it's thought that the pore structures of the zeolites are slightly affected and most of them could be preserved during catalyst preparation and pre-treatment.

The XRD patterns of as-prepared samples reveal the typical characteristics of HZSM-5 (Fig.S2). However, no XRD reflections ascribed to segregated bulk Ga_2O_3 or framework gallium species can be found on these catalyst.²¹ It is probably due to low Ga content, highly dispersed ions and/or extracrystalline oxide-type domain with sizes below 4.0 nm on the external surface.¹⁶ The crystallinities of these materials are determined on the intensity of characteristic peaks ($6.9\text{--}9.1^\circ$ and $22.6\text{--}24.8^\circ$) in XRD patterns. The peak intensity of parent HZSM-5 is highest and its crystallinity is defined as 100%. The crystallinities of other materials depend on the ratios of their strength value of characteristic peaks divided by that of parent HZSM-5. Based on that, crystallinities of the Ga/IM (55.8%),

Ga/IMRO1C (66.4%) and Ga/IMRO3C (72.4%) can be obtained respectively. It is found that crystallinity of the Ga/IM decreases to about 55.8% from original 100% of ZSM-5 dramatically. However, the crystal can be recovered partly through the reduction-oxidation treatment as observed from 66.4% crystallinity of Ga/IMRO1C and 72.4% crystallinity of Ga/IMRO3C, respectively. It's believed that the reduction-oxidation treatment is benefit for preserving the pore structures of the zeolites.

Table 2 shows the bulk and surface compositions of as-prepared catalysts based on the measures of ICP-AES and XPS. As observed, the surface Si/Al ratios of these catalysts decrease and lower than that of the bulk with the introduction of Ga, indicating the enrichment of aluminum on catalyst surface. The increase of aluminum implies that the framework of the Ga modified ZSM-5 zeolites suffers from the dealumination caused by introduction of Ga and the subsequent reduction-oxidation treatment. Therefore, the dealumination of Ga/IMRO1C and Ga/IMRO3C is more severe. Furthermore, it can be seen that the ratios of Si/Ga of the catalysts' surface are lower than that of its bulk. It indicates that the Ga species are enriched on the surface of these catalysts. While higher surface Si/Ga ratios of Ga/IMRO1C and Ga/IMRO3C than that of Ga/IM indicates that the reduction-oxidation treatment is in favor of promoting the entry of the surface Ga into the intracrystalline region/channels of the zeolite.

3.2 DRIFT

To observe the OH stretching change of special groups that exist on the catalyst surface, the as-prepared catalysts are investigated by means of DRIFT, and the results are shown in Fig. 1. In the region from 3400 cm^{-1} to 4000 cm^{-1} , four bands are observed on four samples.^{3, 6} Wherein, (i) the band at 3601 cm^{-1} is ascribed to the stretching vibration of Si(OH)Al bridged bonds, which are associated with the zeolite BAS;^{6, 11} (ii) the band at about 3650 cm^{-1} is ascribed to extra-framework aluminium OH group, which is associated with zeolite LAS;² (iii) the band at 3671 cm^{-1} is assigned to the extra-framework gallium OH group, which is associated with weak LAS;^{2, 22} (iv) the band at 3737 cm^{-1} is attributed to terminal Si-OH group. As observed in Fig. 1, the intensity of the peak at 3601 cm^{-1} on Ga/IM declines with Ga incorporation to HZSM-5, suggesting that the number of BAS decreases. It is plausible that the decrease results from exchange of the partial acidic protons with ionic gallium species or dealumination of ZSM-5 zeolites.⁷ Moreover, a further reduction in intensity of the 3601 cm^{-1} peak occurs on Ga/IMRO1C and Ga/IMRO3C, implying that the reduction-oxidation treatment also leads to the decrease of BAS. While the intensity of the peak close to 3650 cm^{-1} on Ga-containing ZSM-5 zeolites especially for Ga/IMRO1C and Ga/IMRO3C increases in contrast with that on HZSM-5, the spectra indicate that the dealumination has occurred with Ga incorporation to HZSM-5 and is aggravated by subsequent reduction-oxidation treatment, as previously verified by the results of XPS in Table. 2. Furthermore, somewhat increase in intensity of the peak at 3671 cm^{-1} on Ga-containing ZSM-5 zeolites is not obvious, probably because part of the peak is concealed by peak of Al-OH and more surface Ga enter into the intracrystalline region/channels of zeolites by reduction-oxidation treatment.

3.3 Py-FTIR.

FTIR spectra of pyridine adsorption on different catalysts are recorded to identify the BAS and LAS, and the quantified results of different types of acid sites are shown in Fig. 2. It is noted that there are three adsorption peaks of pyridine at $\sim 1450\text{ cm}^{-1}$, $\sim 1490\text{ cm}^{-1}$ and $\sim 1540\text{ cm}^{-1}$, which are assigned to the characteristic bands of LAS, the co-contribution of LAS and BAS, and BAS respectively (as shown in Fig. 2A).¹¹ As seen in Fig. 2B, the number of BAS decreases with the elevated evacuation temperature for all as-prepared samples. It implies that both weak and strong BAS are present on these catalysts. Compared with HZSM-5, Ga/IM shows a slight decline in the number of BAS somewhat. And the decline in BAS is greatly deteriorated when Ga/IM is treated with reduction-oxidation as that of Ga/IMRO1C and Ga/IMRO3C in Fig. 2B. The results are consistent with the previous infrared results in the OH stretching region. The concentration of pyridine adsorption on LAS of the catalysts as a function of evacuation temperature is shown in Fig. 2C. The figure shows that pyridine adsorbed on LAS of HZSM-5 disappears substantially after evacuation at $250\text{ }^{\circ}\text{C}$. However, as for Ga/IMRO1C and Ga/IMRO3C, pyridine absorption is still present even at temperatures as high as $450\text{ }^{\circ}\text{C}$, indicating that strong LAS are generated as a result of Ga incorporation via the subsequent reduction-oxidation treatment. Previous work^{11, 23-26} reported that the incorporation of highly dispersed Ga species to ZSM-5 zeolites could promote the formation of strong LAS, which improved dehydrogenation ability of the catalysts. That's to say, the reduction-oxidation treatment to Ga/IM enhances the formation of highly dispersed Ga species contributing to strong LAS. Moreover, the numbers of BAS and the numbers of LAS over the Ga/HZSM-5 catalysts prepared by reduction-oxidation treatment are higher than the Ga/HZSM-5 catalysts prepared by previous treatment (formic acid impregnation and *in-situ* treatment).¹³ That's because the reduction-oxidation treatment leads to less damage of framework of catalysts. From Fig. 2D, it can be observed that pure HZSM-5 has the largest ratio of Brønsted acid concentration/Lewis acid concentration, indicating that large amounts of BAS are present on its surface. However, the ratio decreases with Ga incorporation (such as Ga/IM). Furthermore, the decrease is very dramatic after the subsequent reduction-oxidation treatment as Ga/IMRO1C and Ga/IMRO3C show. Previous research^{4, 27} suggested that BAS of HZSM-5 are exclusive active sites for propane aromatization during whole reaction, while the LAS associated with extra-framework aluminium OH do not contribute to the propane aromatization. However, our prepared Ga/IMRO1C and Ga/IMRO3C exhibited higher conversion of propane and selectivity of BTX than Ga/IM and HZSM-5 as shown in Fig. 3. In combination with other^{4, 11} and our previous reports¹³, it can be deduced that the formed strong LAS by Ga modification to HZSM-5 is equally important for propane aromatization. It can be concluded apparently that the synergy effect between strong LAS related to highly dispersed Ga species and BAS on Ga/IMRO1C and Ga/IMRO3C contributes to propane aromatization activity rather than exclusive effect of BAS.

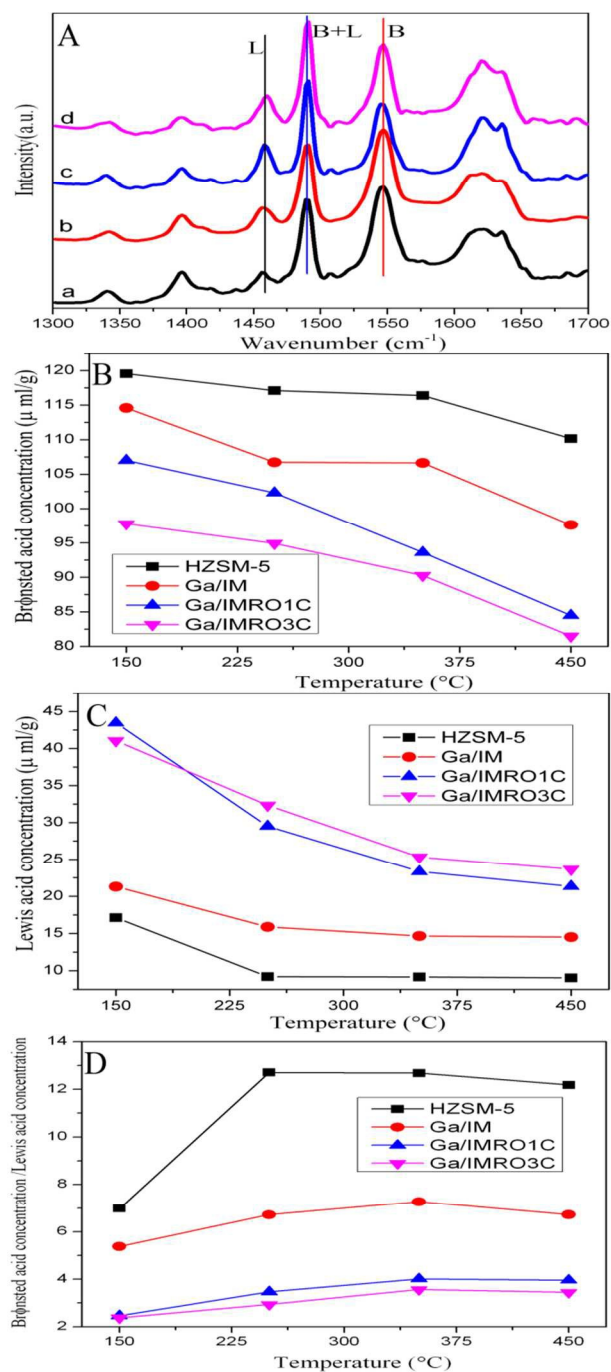


Fig. 2 FTIR spectra of the pyridine adsorption on the catalysts and the quantified results of different acid sites. (A) Spectrum of HZSM-5 (a), Ga/IM (b), Ga/IMRO1C (c) and Ga/IMRO3C (d) after evacuation at $450\text{ }^{\circ}\text{C}$; (B) Brønsted acid site concentration of samples at different temperatures; (C) Lewis acid concentration of samples at different temperatures; (D) Brønsted acid concentration/Lewis acid concentration ratios of samples at different temperatures.

3.4 NH_3 -TPD.

Shown in Fig. 4 are the NH_3 -TPD profiles recorded over as-prepared catalysts. As observed, all catalysts show two desorption peaks of NH_3 (centred at $150\text{--}340\text{ }^{\circ}\text{C}$ and $360\text{--}570\text{ }^{\circ}\text{C}$), which are associated with weak acid sites and strong acid sites, respectively. Compared with two desorption peaks on HZSM-5, that on the Ga-containing ZSM-5 zeolites don't show an obvious shift,

indicating that the incorporation of Ga to HZSM-5 induces little change of acid strength. On the other hand, one can note that the intensity of desorption peaks at 150-340 °C on the Ga-containing samples show a slight decline in comparison with that on HZSM-5, while the intensity of the desorption peak at 360-590 °C on Ga/IMRO1C and Ga/IMRO3C dramatically declines. It also can be further confirmed based on the data of the quantified acid sites as listed in Table S1. The above result suggests that the present method of preparing catalyst can reduce the amount of total acid sites obviously, and most of the decrease is caused by the removal of partial strong acid sites, which is actually associated with the BAS of the catalysts. Thus, it's realized that the decrease of the strong acid sites ascribed to BAS is mainly due to the dealumination of ZSM-5 zeolite and the exchange of BAS' acidic proton with Ga species.⁷ The results are consistent with previous Py-IR results. Moreover, the numbers of strong acid sites over the Ga/HZSM-5 catalysts treated by reduction-oxidation is more than that over the Ga/HZSM-5 catalysts prepared by the previous treatment,¹³ because the reduction-oxidation causes less dealumination of framework and decrease of BAS.

3.5 H₂-TPR.

H₂-TPR profiles of as-prepared samples are depicted in Fig. 5, which show the Ga species evolution for each sample. The pure Ga₂O₃ exhibits two reduction peaks at about 507 °C and 771 °C, which are ascribed to small Ga₂O₃ particles and segregated bulk Ga₂O₃, respectively.³ While Ga/IM shows three reduction peaks centred at about 528 °C, 671 °C and 810 °C, which are assigned to the small Ga₂O₃ particles, highly dispersed gallyl ion species probably (GaO)⁺ and segregated bulk Ga₂O₃ respectively, according to previous research.^{3, 9, 21, 28, 29} In case of Ga/IMRO1C and Ga/IMRO3C, there are only two reduction peaks observed (centred at about 514-522 °C and 633-692 °C) and the peak ascribed to the segregated bulk Ga₂O₃ turns to disappear. It is thought that the segregated bulk Ga₂O₃ can be disassembled into smaller Ga₂O₃ particles on the ZSM-5 zeolite host as well as formation of well-dispersion gallyl ion species via the reduction-oxidation treatment. Through fitting the TPR profiles and calculating their peak areas (Table S2), it is found that the (GaO)⁺ content of Ga/IMRO1C and Ga/IMRO3C are higher than that of the Ga/IM, implying that the reduction-oxidation treatment promotes the formation of highly dispersed (GaO)⁺ species. This is further verified by XPS results. From the characterization of XPS (Fig. S3), it is noted that the Ga 2p_{3/2} binding energy (BEs) of Ga/IM (1119.1eV) is higher than that for Ga₂O₃ (1117.9 eV), indicating a strong interaction between the ionized Ga species and ZSM-5 zeolite. However, Ga 2p_{3/2} BEs for the Ga/IMRO3C ((1118.6 eV)) and Ga/IMRO1C ((1118.8 eV)) are lower than that for Ga/IM. It is because the reduction-oxidation treatment to Ga/IM promotes the formation of (GaO)⁺ species easily and induces the strong covalent character bonding between the highly dispersed (GaO)⁺ species and the framework of the ZSM-5.³ It also has been proved that highly dispersed (GaO)⁺ species which could exchange acidic protons of BAS of the zeolite framework, contributing to the strong LAS.¹¹ The results are concordant with the Py-FTIR results that there are more numbers of strong LAS on Ga/IMRO1C and Ga/IMRO3C.

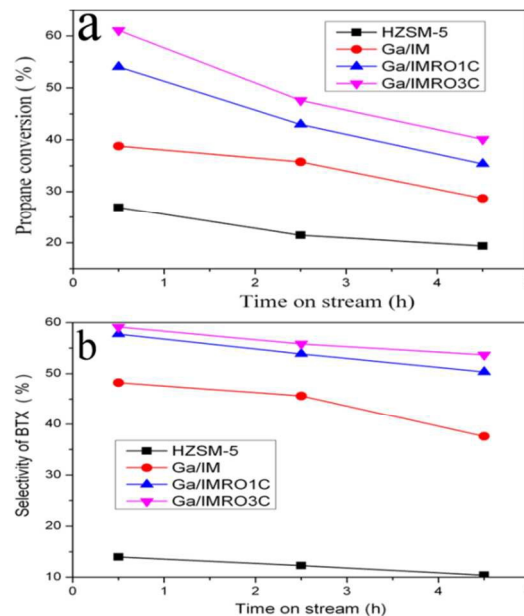


Fig. 3 Propane conversion (a) and selectivity of BTX (b) as a function of time on stream for as-prepared catalysts. Reaction conditions: P = 100 kPa, T = 540 °C, WHSV = 6000 ml/(g·h) and N₂/C₃H₈ molar ratio = 2.

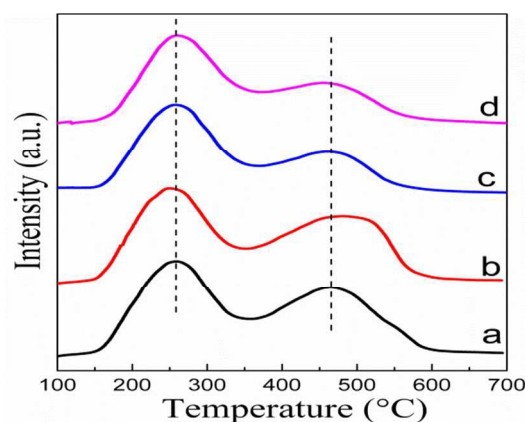


Fig. 4 NH₃-TPD profiles of different catalysts. (a) HZSM-5; (b) Ga/IM; (c) Ga/IMRO1C; (d) Ga/IMRO3C.

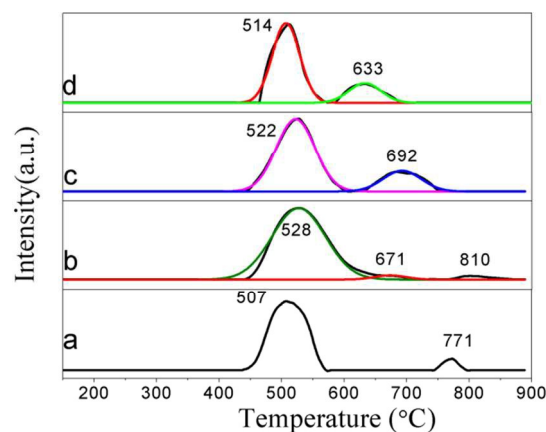


Fig. 5 H₂-TPR profiles of different samples. (a) Ga₂O₃; (b) Ga/IM; (c) Ga/IMRO1C; (d) Ga/IMRO3C.

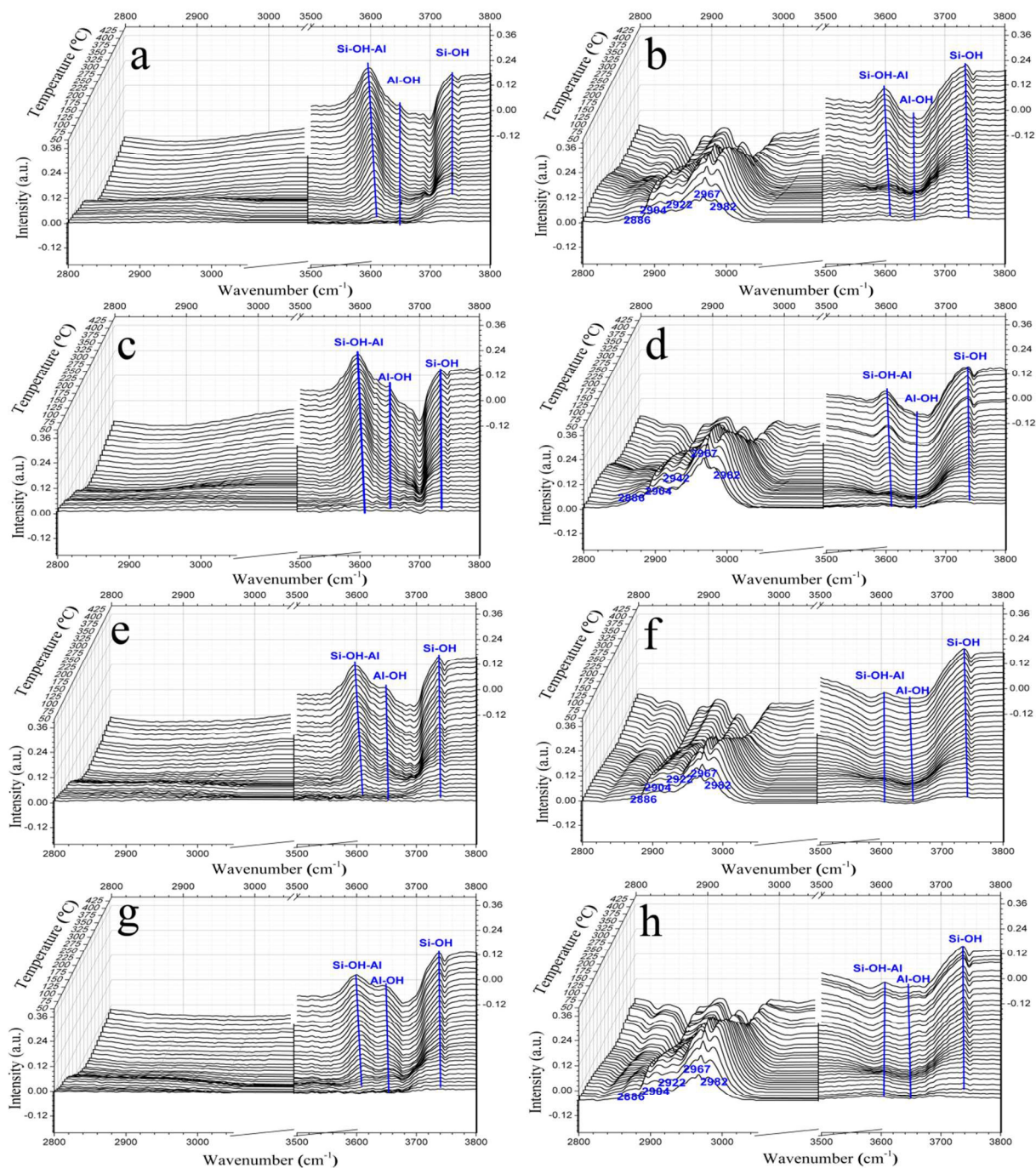


Fig. 6 (a-h) DRIFT spectra of as-prepared samples during TPSR experiment from 50 to 450 °C at the region 2800-3800 cm^{-1} . (a) HZSM-5 (without introduction of propane); (b) HZSM-5; (c) Ga/IM (without introduction of propane); (d) Ga/IM; (e) Ga/IMRO1C (without introduction of propane); (f) Ga/IMRO1C; (g) Ga/IMRO3C (without introduction of propane); (h) Ga/IMRO3C.

3.6 TPSR experiment

TPSR is an important technique to study the surface reaction mechanisms of supported metal catalysts,³⁰⁻³⁶ because it can monitor the evolution of species instantaneously and obtain lots of visualized information during reactions directly. Therefore, in this research, DRIFTS-TPSR and MS-TPSR are used to investigate the mechanistic details in propane aromatization reaction.

In combination with these DRIFT, FTIR, XPS, NH_3 -TPD

data, we pay more attention to study systematically how acidity of Ga/HZSM-5 catalyst affects the evolution of reactants, intermediates and products on the surface of Ga/HZSM-5 as well as the sorption/desorption process by means of DRIFTS-TPSR and MS-TPSR.

DRIFT-TPSR. The DRIFT spectra of different catalysts during TPSR experiment are shown in Fig. 6b, 6d, 6f and 6h, and DRIFT spectra of TPSR experiment without introduction of propane are also shown for comparison in Fig. 6a, 6c, 6e and 6g. As observed

in Fig. 6b, 6d, 6f and 6h, multiple absorption peaks (at about 2886 cm^{-1} , 2904 cm^{-1} , 2922 cm^{-1} , 2967 cm^{-1} and 2982 cm^{-1}) over HZSM-5, Ga/IM, Ga/IMRO1C and Ga/IMRO3C appear in a wide region within 2800-3000 cm^{-1} when the propane is introduced to *in-situ* infrared cell in which the catalyst is placed. These peaks are assigned to the adsorbed alkyl species which are characteristic of ethyl and/or methyl groups bonded to Ga.^{37, 38} While, other bands such as 2819 cm^{-1} , 2844 cm^{-1} and 2856 cm^{-1} probably are assigned to the C-H stretching of those alkanes with three or more carbon atoms such as propyl, butyl and so on.^{37, 38} Therefore, it's plausible that the bands in the 2800-3000 cm^{-1} should be assigned to the C-H stretching of propane as well as the intermediates such as methane, ethane, etc. Simultaneously, it can be seen that the intensity of these peaks (at about 2886 cm^{-1} , 2904 cm^{-1} , 2922 cm^{-1} , 2967 cm^{-1} and 2982 cm^{-1}) over HZSM-5, Ga/IM, Ga/IMRO1C and Ga/IMRO3C firstly increases with enhanced temperature until about 125 °C and then decreases as a function of temperature (this is also observed based on the profiles of the peak intensity as a function of temperature in Fig. S4). Within the reaction temperature of 50-125 °C, the dehydrogenation and β -scission of propane occur mainly with the increase of temperature, accordingly forming the intermediates with ethyl and/or methyl groups such as methane, ethane, ethylene, etc. However, when reaction temperature is further elevated (>125 °C), the formed intermediate species are quickly and easily converted to higher carbon products such as butane, BTX aromatics, etc. This suggests that propane aromatization is strongly affected by temperature. In another peak region: around 3500-3800 cm^{-1} , it is also found that there are three hydroxyl (-OH) vibration peaks centred at 3601 cm^{-1} , 3650 cm^{-1} and 3737 cm^{-1} from Fig. 6a, 6c, 6e and 6g, which are ascribed to the stretch of Si(OH)Al group, extra-framework Al-OH group and extra-framework Si-OH group respectively. The intensity of the peaks increases with the elevation of temperature, which indicates an enhanced thermal vibration of chemical bond as a function of temperature. In addition, a reduction in peak intensity of Si(OH)Al group can be observed with Ga introduction to HZSM-5 zeolite, indicating a decreased amounts of BAS.⁷ While the peak intensity of Al-OH group is enhanced as well as the appearance of Ga-OH group with Ga incorporation. The results are consistent with the previous DRIFT results. However, when propane was introduced into catalytic system, the peak intensities of Si(OH)Al group associated with BAS and Al-OH group associated with LAS for these catalysts decline to different extents as shown in Fig. 6b, 6d, 6f and 6h. Especially for Si(OH)Al group, the decrease is very severe. Yet Si-OH group with little acidity show no decline in peak intensity. The results imply that propane and intermediates are more facilely adsorbed on the acid sites, especially on the strong acid sites.³⁹⁻⁴¹ From Fig. 6, it's observed that peak intensity of these Si(OH)Al, Al-OH, and Si-OH groups over as-prepared catalysts change with the increase of temperature accordingly. As is well known, the peak intensity could reflect the relative amount of the groups on catalyst surface, which is useful to reveal the acidic properties of catalyst. However, it is very difficult to observe the obvious difference of the peak intensity with various temperatures. In order to calculate accurately the intensity of each peak, the DRIFT spectra of these samples from 3500 cm^{-1} to 3800 cm^{-1} are

deconvoluted. Different hydroxyl (-OH) stretching groups (Si(OH)Al, Al-OH, Ga-OH and Si-OH) are identified from four peaks with the following wavenumbers: 3601 cm^{-1} , 3650 cm^{-1} , 3671 cm^{-1} and 3737 cm^{-1} respectively, by deconvolution of the experimental spectra with Gaussian peaks ($R^2 > 0.99$) after deducting the base line. The peak intensities of these bands (at 3601 cm^{-1} , 3650 cm^{-1} , 3671 cm^{-1} and 3737 cm^{-1}) over the catalysts as a function of temperature are plotted and the profiles are displayed in Fig. S5. As observed, the intensities of Si(OH)Al peaks over these Ga-containing ZSM-5 catalysts (Fig. S5d, S5f and S5h) are lower than that over HZSM-5 (Fig. S5b) while the intensities of Al-OH peaks are somewhat higher. Moreover, with introduction of propane to this catalytic system (S5b, S5d, S5f, S5h), the intensities of Si(OH)Al peaks and Al-OH peaks over these catalysts decrease especially for the Si(OH)Al peaks, while the intensities of Si-OH peaks show little increase. It is probable that the decrease is caused by adsorption of propane and intermediates on the acid sites ascribed to Si(OH)Al group and Al-OH group. This is accordant with the conclusion obtained from Fig. 6. The intensity of Ga-OH peak at 3671 cm^{-1} as a function of temperature is also investigated. It can be seen from Fig. S5 that the intensity of Ga-OH group on the Ga modified ZSM-5 zeolites is similar to Al-OH group, implying that Ga-OH group which shows weak Lewis acidity is also the sorption center for propane and intermediates probably.²²

In addition, it's difficult to detect the characteristic peak of GaO^+ species by infrared spectroscopy even using probe molecules such as carbon monoxide,¹⁰ but the scientific recognition that highly dispersed (GaO^+) species are present on Ga/IMRO1C and Ga/IMRO3C has been verified as a result of the impregnated incorporation of Ga and subsequent reduction-oxidation treatment, inferred from previous Py-FTIR, H_2 -TPR and XPS results. As thought,¹¹ the (GaO^+) species can exchange with acidic protons of BAS, generating the strong LAS. We deduce that the strong LAS should be the sorption centers for propane and intermediates based on the strong sorption of propane and intermediates on the strong acid sites as above shown.

Conclusively, the above results indicate that the sorption of propane and intermediates mainly occurs on acid sites, especially on strong acid sites. Meanwhile, the generated strong LAS related to highly dispersed Ga species and BAS on ZSM-5 zeolites have a synergistic effect on sorption/desorption processes of propane and intermediates.

MS-TPSR. Propane-TPSR profiles for as-prepared catalysts are shown in Fig. 7. These profiles are divided into three temperature regions: 150–270 °C (temperature region I), 270–400 °C (temperature region II) and 400–550 °C (temperature region III). In every temperature region, the detail information (formation temperatures and peak intensity) of main desired reactant and products (propane, methane, ethylene, propylene, hydrogen, benzene, toluene and xylene) are collected and listed in Table S3, Table S4, Table S5 and Table S6 respectively. As observed in Fig. 7a, the desorption peaks of propane, methane, ethylene, propylene and hydrogen over HZSM-5 appear in the region I. According to the literatures,^{4, 27} it could be understandable that the propylene was generated from dehydrogenation of propane

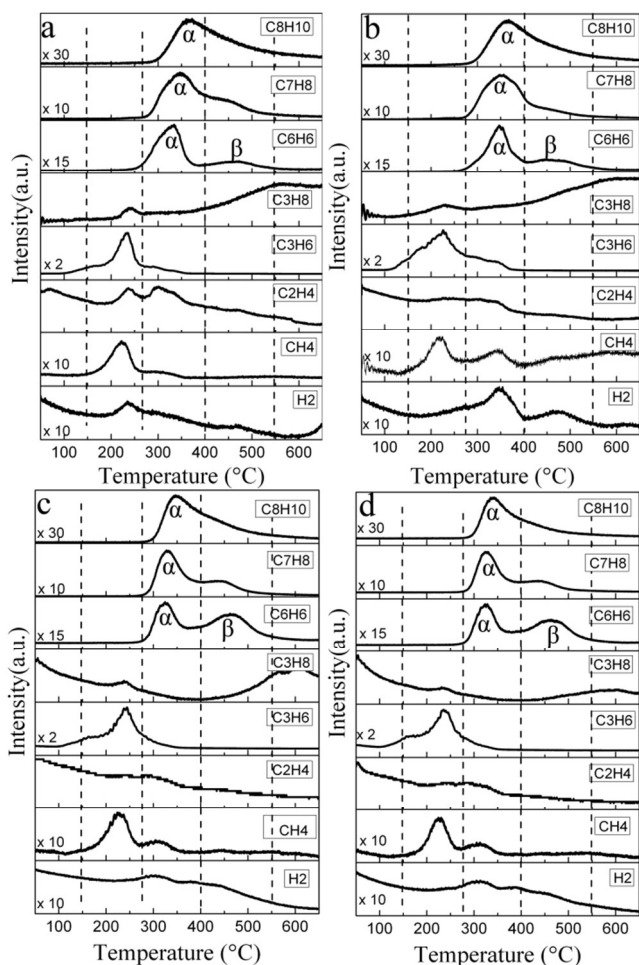
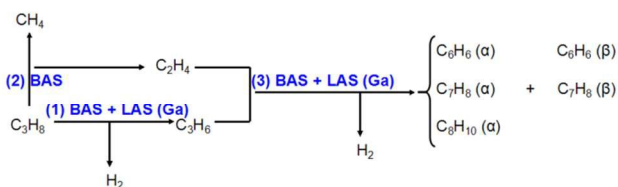


Fig. 7(a-d) Propane-TPSR profiles for as-prepared catalysts. (a) HZSM-5; (b) Ga/IM; (c) Ga/IM RO1C; (d) Ga/IMRO3C.



Scheme 1 Main reaction pathway for propane transformation over Ga/HZSM-5. Step (1) dehydrogenation of propane to propylene; Step (2) β -scission of propane to methane and ethylene; Step (3) conversion of propylene and ethylene to benzene, toluene and xylene.

with release of hydrogen while methane was produced from β -scission of propane accompanied by ethylene release at the primary stage of propane aromatization. Here, dehydrogenation and β -scission of propane almost occur instantaneously based on the close starting formation temperatures of methane and propylene. As for region II and III in Fig. 7a, the BTX can be observed, indicating the occurrence of aromatization reaction. It has been previously accepted that the propylene and ethylene are primary intermediates for producing BTX aromatics. Therefore, it's deduced that, in present TPSR experiment, a part of the formed propylene and ethylene in region I desorbs from catalyst surface while another part is further converted into benzene,

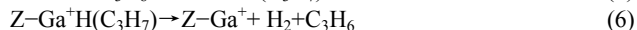
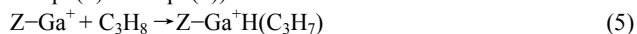
toluene and xylene with the elevated temperature by a series of processes such as dehydrogenation, cyclization and aromatization. It is apparent that no less than two active sites for propane aromatization exist on the pure HZSM-5. Wherein, one kind of active sites contribute to the generation of propylene and ethylene only, and another kind of active sites turn to contribute to two processes containing the generation of propylene and ethylene and their aromatization to BTX. As for Ga-containing ZSM-5 zeolites (Fig. 7b, 7c, 7d), the distribution and adscription of the peaks are similar to that of HZSM-5, but the peak intensity and formation temperature of the products such as hydrogen, ethylene, BTX, etc. are tremendously different. The methane and ethylene both come from the β -scission of propane over Ga/IM, Ga/IMRO1C and Ga/IMRO3C as HZSM-5 shows. But, only trace amount of ethylene can be observed on Ga/IM, Ga/IMRO1C and Ga/IMRO3C in region II and III (as shown in Fig. 7b, 7c and 7d). Because most of the formed intermediate ethylene obtained by the β -scission of propane over these Ga-containing ZSM-5 catalysts can be converted to BTX product rapidly considering that ethylene and propylene aromatization is quite an easy process. Hence, the result that the amount of ethylene over HZSM-5 is more than that over other Ga-containing ZSM-5 catalysts is due to lower activity of HZSM-5 in aromatization. Compared with the peak intensity of hydrogen over HZSM-5, that over the Ga/IM is obviously enhanced in region II and III (as shown in Fig. 7b and Table S4), indicating that the incorporation of Ga promotes the dehydrogenation of propane and intermediates to form BTX. In case of Ga/IMRO1C and Ga/IMRO3C, the peak intensity of hydrogen in region II and III is also enhanced as that of Ga/IM. In fact, through curve-fitting results of the detected hydrogen and benzene profiles for the catalysts (Fig. S6), it is notable that Ga/IMRO1C and Ga/IMRO3C show an additional dehydrogenation peak (defined as θ peak) except those peaks (α , β , γ) as shown in Fig. S6a. It is plausible that the appearance of the θ peak caused by the reduction-oxidation treatment is closely relative with the improved dehydrogenation behavior of Ga/IMRO1C and Ga/IMRO3C. Based on a slight shift of the peaks of benzene (α state), toluene (α state) and xylene (α state) to higher temperature over the Ga/IM than that over the HZSM-5, it is thought that the impregnated incorporation of Ga can lead to an increase of aromatization temperature. As observed in Fig. 7c, the peaks of products such as benzene (α state), toluene (α state) and xylene (α state) over the Ga/IMRO1C shift to lower temperatures by 25°C, 25°C and 18°C (Table. S5) respectively, compared to that over Ga/IM. This suggests that the benzene (α state), toluene (α state) and xylene (α state) are more facily generated on Ga/IMRO1C at lower temperature than Ga/IM. Besides, it can also be found that the peak intensity of benzene on Ga/IMRO1C increases in region III in contrast with that on Ga/IM (Fig. 7c and Fig. S6b), which implies that more benzene (β state) are generated on Ga/IMRO1C. The case of Ga/IMRO3C catalyst is similar to Ga/IMRO1C (as shown in Fig. 7d and Table S6) except a slight difference on temperature shift.

Propane aromatization belongs to a tandem process and contains a series of steps, such as dehydrogenation and β -scission of propane to propylene and ethylene, oligomerization and interconversion of olefins, olefin alkylation, cyclization and

aromatization.^{4,27} Here, each step during the reaction is affected by the acidity of catalysts. The DRIFTS-TPSR results have suggested that the sorption of propane and intermediates mainly occurred on acid sites such as BAS related to Si(OH)Al group and LAS associated with Al-OH group over ZSM-5 zeolites. And previous researches^{4,27} also showed that the BAS over ZSM-5 zeolite were exclusive active sites for propane aromatization on pure HZSM-5, contributing to the whole processes of propane aromatization, while LAS over ZSM-5 zeolites were only sorption centers. In the Py-FTIR results in Fig. 2D, we observe that the ratios of Brønsted acid concentration/Lewis acid concentration for HZSM-5 are greater than 6.0 at all evacuation temperatures, while the ratio of weak acid site/strong acid site is 1.2 (Table S1). This indicates that BAS over ZSM-5 zeolite are comprised of the weak and strong BAS, which probably correspond to two kinds of active sites above-mentioned from MS-TPSR results. As thought, both the dehydrogenation of propane to propylene and β -scission of propane to methane and ethylene occur on the weak and strong BAS over HZSM-5 at low temperature. With the elevation of reaction temperature, a part of generated propylene and ethylene on strong BAS are further converted into BTX aromatics. In our present catalytic system, actually the acid properties of catalyst have a remarkably close relation with Ga incorporation. Introduction of Ga to ZSM-5 zeolite can lead to a modest decline in the number of BAS, which is caused by the exchange of BAS' acidic protons with Ga species and dealumination of ZSM-5 zeolite, and the generation of more LAS related to Ga species. As for Ga/IM, the addition of Ga³⁺ ions into ZSM-5 intercrystalline is very difficult because of the highly positive electrostatic charge and the bulky size of [Ga(H₂O)₆]³⁺ aquacomplexes, and thus Ga³⁺ ions tend to reside predominantly on the external surface of zeolite as single extracrystalline Ga₂O₃.⁴² It has been verified that the extracrystalline Ga₂O₃ species have relatively low activity in propane aromatization, because their activation is remarkably complicated and difficult. Al-Yassir and Rane *et al.*^{2,10} thought that the active species were formed through two main processes: *in-situ* reduction of extracrystalline Ga₂O₃ to the highly mobile Ga₂O by H₂ or hydrocarbons in the feed and subsequent interaction with BAS to form a Z-Ga⁺ structure (Z⁻ represents an ion-exchange site at the zeolite framework) as show in eqn (3) and eqn (4).



And the Z-Ga⁺ structure can catalyze propane to propylene as well as subsequent aromatization via dehydrogenation (as shown in eqn (5) and eqn (6)).¹⁰



In case of Ga/IMRO1C and Ga/IMRO3C, activation of Ga species relatively facilely proceeds. The reduction-oxidation treatment promotes the formation of these highly dispersed Ga species probably (GaO)⁺. After exchanging with acidic protons of BAS, the (GaO)⁺ species are anchored to ZSM-5 zeolite to form the structures of Z-GaO⁺ which are ascribed to strong LAS. Finally, Z-Ga⁺ structure is easily obtained via the deoxygenation of Z-GaO⁺ by in hydrocarbons or H₂ flow (as show in eqn (7)).¹⁰



Therefore, it is apparent that the generated strong LAS related to highly dispersed Ga species are active centers for propane and intermediates on Ga/IMRO1C and Ga/IMRO3C for aromatization reaction. According to previous research,¹¹ these strong LAS play a key part in dehydrogenation process, while BAS are responsible for the whole aromatization processes. Over Ga/IMRO1C and Ga/IMRO3C, dehydrogenation of propane to propylene occurs on the BAS and strong LAS at low temperature in propane-TPSR experiment, while β -scission of propane to methane and ethylene only occurs on BAS. With elevation of temperature, the generated propylene and ethylene are further converted into BTX aromatics with release of hydrogen on strong BAS and strong LAS. Based on present TPSR results and our discussion, a new and main reaction pathway for propane transformation is well designed as shown in Scheme1.

Apart from that, the incorporation of Ga adds a new dehydrogenation route in propane aromatization and improves dehydrogenation ability of the Ga-containing ZSM-5 zeolites inferred from the above discussion.⁴ This is further verified by the MS-TPSR results that the peak intensity of hydrogen over Ga-containing ZSM-5 zeolites is obviously enhanced in region II and III with Ga incorporation to HZSM-5. Furthermore, the reduction-oxidation treatment to Ga/IM promotes the formation of strong LAS, which are probably responsible for the generation of the additional θ dehydrogenation peak on Ga/IMRO1C and Ga/IMRO3C. And the strong LAS could enhance dehydrogenation steps tremendously in propane aromatization reaction, including the dehydrogenation of propane to propylene and the conversion of propylene and ethylene to BTX aromatics. It's concluded that the synergistic effect between strong LAS and BAS on Ga/IMRO1C and Ga/IMRO3C contributes to dehydrogenation and β -scission of propane as well as subsequent aromatization reaction process. It's the synergistic reaction between these two kinds of acid sites that results in lower aromatization temperature and larger amounts of product of benzene (β state) on Ga/IMRO1C and Ga/IMRO3C than that over Ga/IM. That may be the reason that Ga/IMRO1C and Ga/IMRO3C show higher catalytic performance for propane aromatization than HZSM-5 and Ga/IM as show in Fig. 3.

4. Conclusion remarks

The Ga-modified HZSM-5 precursors (Ga/IM), containing 1 wt % Ga, was prepared by incipient wetness impregnation method, and then subjected to one- or three-time treatment of reduction in hydrogen and re-oxidation in air. The resulting Ga/IMRO1C and Ga/IMRO3C catalysts were characterized by the techniques such as N₂ physical adsorption, ICP-AES, DRIFT, Py-FTIR, NH₃-TPD, H₂-TPR, XPS, DRIFT-TPSR and MS-TPSR to understand the correlations between acidity of these catalysts and their activity for propane aromatization. The characterization data suggested that the impregnated introduction of Ga to ZSM-5 zeolite and subsequent reduction-oxidation treatment led to a great decline in the numbers of BAS because of and the exchange of BAS' acidic protons with Ga species as well as the severe dealumination of ZSM-5 framework, and thus promoted facilely the formation of strong LAS attributed to highly dispersed Ga species probably (GaO)⁺ over Ga/IMRO1C and the Ga/IMRO3C in comparison with that over Ga/IM. On the other hand, both the

BAS and strong LAS were the sorption centers and reaction centers for propane and its intermediates. The strong LAS were expert in promoting dehydrogenation steps during propane aromatization, while the BAS are responsible for the whole aromatization processes. According to TPSR results, the dehydrogenation of propane to propylene occurs on BAS and strong LAS, while β -scission of propane to methane and ethylene only occurs on BAS at low temperature. With the elevation of temperature, part of generated propylene and ethylene on the strong BAS and strong LAS were further converted into BTX aromatics with release of hydrogen. It was plausible that the synergistic effect between BAS and strong LAS contributed to lower aromatization temperature of propane into BTX and more product of benzene (β state) over Ga/IMRO1C and Ga/IMRO3C than that over the Ga/IM.

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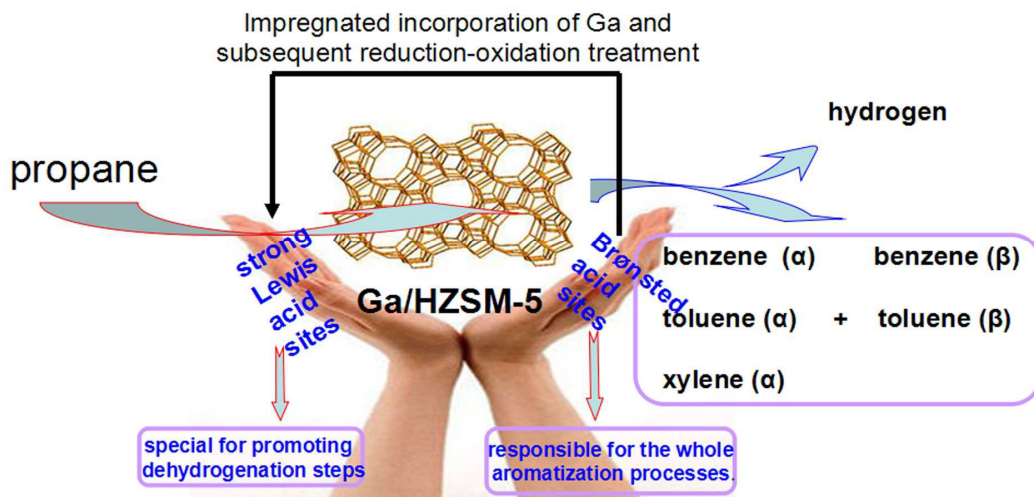
^a State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, China;

^b University of Chinese Academy of Sciences, Beijing 100049, China.

^c E-mail: tan@sxicc.ac.cn. Tel: +86-351-4044287. Fax: +86-351-4044287.

Supplementary text; Fig.S1-S4; Table S1-S6. See DOI: 10.1039/b000000x/

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Mechanistic insight to synergistic effect between Brønsted acidity and strong Lewis acidity of Ga/HZSM-5 on its activity for propane aromatization