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ARTICLE TYPE

A highly efficient Ga/ZSM-5 catalyst prepared by formic acid impregnation and in-situ treatment for propane aromatization

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A simple method for the preparation of a Ga/ZSM-5 catalyst for propane aromatization was established by formic acid impregnation and *in-situ* treatment. The catalyst prepared by this novel method showed remarkably superior activity of propane aromatization. Under the conditions: T = 540 °C, P = 100 kPa, WHSV = 6000 ml/(g·h) and with a N_2/C_3H_8 molar ratio of 2, the highest propane conversion and selectivity of BTX (benzene, toluene and xylene) on H-Ga/SNSA catalyst achieved was 53.6% and 58.0% respectively, much higher than that of the catalyst prepared using traditional impregnation method (38.8% and 48.2%). The catalysts were characterized by nitrogen physical adsorption, ICP-AES, DRIFT, Py-FTIR, NH_3-TPD, H_2-TPR, XPS and ^{27}Al MAS NMR techniques. The characterization data indicated that this facile methodology enhanced the dispersion of Ga species and promoted the formation of highly dispersed $(GaO)^+$ species, which could exchange acidic protons (Brønsted acid sites) of the zeolite framework contributing to the strong Lewis acidity. The super catalytic behavior was attributed to the synergistic effect between strong Lewis acid sites generated by the $(GaO)^+$ species and the Brønsted acid sites.

1. Introduction

Propane (light alkane) aromatization plays an important role in economic and strategic fields[1] and has been extensively studied in recent years. In this process, Zn[2], Pt[3, 4] and Ga[5-9] modified ZSM-5 zeolites are currently used as the catalysts for propane aromatization based on their superior catalytic performance over other catalysts. Considering the deactivation of Pt/ZSM-5 and the poor stability of Zn/ZSM-5 in propane aromatization—induced by rapid coke deposition and the loss of the active component (especially for Zn loaded catalysts)[9]—research turned to focus on Ga modified ZSM-5 catalysts for aromatization. Research has shown that the structure, position and state of the Ga species on the catalyst correlates closely to the preparation method and treatment process, which in turn has a strong effect on the propane aromatization performance—though the understanding of the active Ga species catalytic mechanisms still divide the scientific community.[10, 11] A series of methods such as hydrothermal *in-situ* synthesis and post synthesis (ion-exchange, impregnation, chemical vapour deposition [CVD] and reduction-oxidation cycles), have been developed to prepare highly efficient Ga modified ZSM-5 catalysts for propane aromatization. Choudhary *et al.*[12-16] prepared a well-established H-galloaluminosilicate (H-GaMFI) catalyst for propane aromatization using a one-step hydrothermal synthesis method. Their findings of the superior activity of the catalyst were attributed to its relatively strong acidity and uniform distribution of extra framework Ga-oxide species in the zeolite channels. Al-Yassir *et al.*[17] mixed a hydrothermally treated H-GaMFI zeolite with an aqueous solution of hexadecyltrimethylammonium bromide (CTAB) and further induced a second hydrothermal treatment resulting in a new catalyst. The activity tests reported improved catalytic performance when converting propane to aromatics when compared with the conventional hydrothermally once-treated H-GaMFI catalyst. The authors postulated that the addition of CTAB led to ordered mesopores in the H-GaMFI zeolite, which effectively facilitated the ingress of Ga_2O_3 into the micropores during the second hydrothermal treatment forming extra framework Ga species being highly active for alkane aromatization. Kwak *et al.*[18] prepared a Ga/ZSM-5 catalyst for aromatization using a CVD method together with subsequent H_2 treatment. The results suggested this method allowed Ga to migrate into the zeolite channels efficiently thereby improving alkane aromatization activity. Hensen *et al.*[19] prepared Ga/ZSM-5 by CVD of Ga-alkyl species including, trimethylgallium ($Ga(CH_3)_3$) and the dimethylgallium analogue, on a ZSM-5 zeolite host and studied the activation of the latter precursor to reduced and oxidized species by *in-situ* Ga K edge XANES. It found that the intended reduction-oxidation treatment to these Ga-alkyl species on the catalyst led to the formation of Ga^{3+} species in the form of $(GaO)^+$ coordinating to the zeolite framework which acted as the active sites for the aromatization of propane. The simple and effective reduction-oxidation cycles method has also been frequently adopted to prepare Ga/ZSM-5 catalysts in recent years typically used for the treatment of H_2-O_2 cycles to sample after the impregnation or ion-exchange with aqueous solutions of gallium salts. Meriaudeau *et al.*[6, 20-24] studied in detail the effect of reduction-oxidation treatment to ion-exchanged Ga/ZSM-5 on the dispersion and state of the Ga species. According to the characterization data, the reduction-oxidation cycles processes were shown to adjust the state of Ga species and thereafter enhance their diffusion into the ZSM-5 zeolite channels, enhancing the dispersed Ga species (such as Ga^+, GaO^+ and to a lesser extent $Ga(OH)^{2+}$) on the catalyst in substitution of framework acidic protons. In addition to the reduction-oxidation cycles treatment, other treatment processes have been shown to increase the dispersion of Ga species on Ga/ZSM-5. Fricke *et al.*[25] reported improvements in Ga dispersion as a function of pH during impregnation. The results of Diakonov *et al.*[26] suggested that the pH and temperature factors of aqueous solutions greatly affect the distribution of Ga species. Under acid impregnation conditions, $Ga(OH)_x^{y+}$ precursors, such as $Ga(OH)_2^+$ and $Ga(OH)^{2+}$ formed and were easily transported into the ZSM-5 zeolite channels, interacting with the acid protons to generate active Ga species.[21] Furthermore, steam treatment is an alternative method to enhance the dispersion of Ga species and promote the formation of extra framework active Ga species.[27]

In this work, a novel method was adopted to prepare a highly active Ga/ZSM-5 catalyst for propane aromatization through improved dispersion and state of the Ga species. The referred to treatment process consists of two steps: pre-treatment (formic acid impregnation) and *in-situ* treatment (calcination under static N_2 atmosphere and treatment of steam generated by decomposition of contained-Ga species such as hydration or hydroxylation compounds, etc. and thermal dehydration of the zeolite catalyst) of HZSM-5. The resulting catalyst was designated as H-Ga/SNSA. The test results indicated that the H-Ga/SNSA exhibited high catalytic performance for propane aromatization in comparison with catalyst prepared by impregnation method. To understand the origin of the enhanced catalytic performance, characterization techniques such as nitrogen physical adsorption, ICP-AES, DRIFT, Py-FTIR, NH_3-TPD, H_2-TPR, XPS and ^{27}Al MAS NMR were used. We found that this novel treatment process improved the Ga dispersion efficiency generating ample extra framework active $(GaO)^+$ species. The superior activity of H-Ga/SNSA was attributed to a synergistic effect between strong Lewis acid sites generated by $(GaO)^+$ species and Brønsted acid sites.

2. Experimental section

2.1 Catalyst preparation

HZSM-5 (silica to aluminium mole ratio = 19) zeolites were bought from Nankai University. The catalysts were prepared as follows. Typically, 3 g of HZSM-5 was added to 5 ml aqueous solution containing 0.11 g of gallium nitrate. The resulted mixture was sonicated for 1 h at room temperature, followed by drying at 120 °C for 8 h, and the obtained precursor defined as Ga/dried. Thereafter, the Ga/dried material was calcined at 540 °C for 5 h under static air in a muffle oven to obtain the Ga/calcined catalyst. Likewise, 0.15 g of the Ga/dried material was pressed and sieved into 30-50 mesh fractions and treated in a micro fixed-bed reactor for 0.5 h with a N_2 flow (15 mL/min) to completely remove other gases and moisture. The reactor was then heated to 540 °C at the ramp rate of 6 °C /min and kept at 540 °C for 1h under static N_2, followed by a N_2 flow (15 mL/min) for 1 h to obtain the Ga/SNSA catalyst.

The precursor to the catalyst in this work, (H-Ga/dried) was prepared as follows. 3 g of HZSM-5 zeolite was added to 5 ml solution of formic acid, which was composed of 0.27 g formic acid and 0.11 g gallium nitrate. The resulting mixture was dried at 120 °C for 8 h after mild sonicating for 1 h. Finally, the H-Ga/SNSA catalyst was prepared by treating the H-Ga/dried material in a micro fixed-bed reactor under the same conditions to that of the above Ga/SNSA. Compared with H-Ga/SNSA, a H-HZ/SNSA catalyst was also prepared by the same method to that of H-Ga/SNSA except for the omission of the gallium nitrate precursor. To considering the factor of pH, two samples, H(half)-Ga/SNSA and H(double)-Ga/SNSA, were also prepared by varying the amount of formic acid to either half or double the original formic acid volume, respectively. In addition, alternative acids such as acetic acid, nitric acid and citric acid were used to determine the impact of the resulting catalysts. This group of catalysts were defined as: H(acetic)-Ga/SNSA, H(nitric)-Ga/SNSA and H(citric)-Ga/SNSA, respectively.

2.2 Catalyst characterization

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

Diffuse reflectance infrared spectra (DRIFT) measurements were performed using a Bruker Tensor 27 instrument with a MCT detector (64 scans, 4 cm^{-1}). Weight approximately 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 argon flow.

Pyridine-adsorbed Fourier Transform Infrared Spectroscopy (Py-FTIR) was used to determine the amount of Brønsted and Lewis acid sites in Bruker Tensor 27 equipment. Approximately 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 (NH_3-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 N_2 (30 ml/min) for 2 h and then cooled down to 100 °C. Then NH_3 was introduced into the flow system. The TPD spectra were recorded at a temperature rising rate of 10 °C/min from 100 °C to 700 °C.

The H_2-Temperature-programmed reduction (H_2-TPR) was carried out to study reducibility of the catalysts with chemisorption instrument (TP-5080). The catalyst (100 mg) was pretreated at 500 °C under a flow of N_2 (32 ml/min) for 1 h and then cooled down to 100 °C, then changed to H_2/N_2 = 0.09 mixture (35 ml/min). The temperature-programmed reduction was performed between 100 °C and 900 °C with a heating rate of 10 °C /min.

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The chemical compositions (Si, Al and Ga) of as-prepared samples were determined by an inductively coupled plasma-atomic emission spectrometer (ICP-AES) method using Thermo iCAP 6300 equipment.

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.

^{27}Al MAS NMR measurements were performed on Bruker AVANCE III 600 MHz equipment. ^{27}Al MAS NMR spectra were obtained by a single pulse length of Π/6, and Al chemical shifts were referenced to $Al(NO_3)_3$.

The thermal gravimetry-mass spectrum (TG-MS) measurements were performed under a flow of argon (30 ml/min) in the temperature range from 120 to 600 °C with a heating rate of 10 °C /min on an Evolution and OMNI star equipment.

2.3 Catalyst evaluation

The catalyst test for propane aromatization 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 N_2/C_3H_8 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 Al_2O_3 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 Eqs. (1) and (2).

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

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

where $X_{propane}$ is the conversion of propane, S_i is the selectivity of target product i (i = BTX, CH_4, 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 Catalytic activity

Fig. 1A and Fig. 1B show the propane conversion and selectivity of BTX (benzene, toluene and xylene) over as-prepared catalysts respectively. The data clearly shows propane conversion and selectivity of BTX over Ga/calcined and H-Ga/SNSA are superior to that over HZSM-5 and H-HZ/SNSA respectively, suggesting the introduction of Ga to ZSM-5 (treated or untreated) improves the catalytic performance. At the same time, it is noticeable that the catalytic activity of H-HZ/SNSA is lower for propane aromatization than that of HZSM-5, while that of H-Ga/SNSA is higher than Ga/calcined and HZSM-5. The catalytic data indicates that this novel treatment process exclusively takes effect on the Ga species rather than the ZSM-5 zeolite as the reason for improved catalytic behavior. Furthermore, Fig. 1 also shows that this simple method is highly efficient for improving Ga activity on modified HZSM-5 when compared with the catalyst prepared by the traditional impregnation method. As observed in Fig.1, Ga/SNSA shows a lower activity for propane aromatization than H-Ga/SNSA, however, the observed activity is higher than Ga/calcined. Therefore the implication is that the formic acid impregnation and *in-situ* treatment play equally important roles in improving the catalytic performance of H-Ga/SNSA, which principally takes effect on the Ga species.

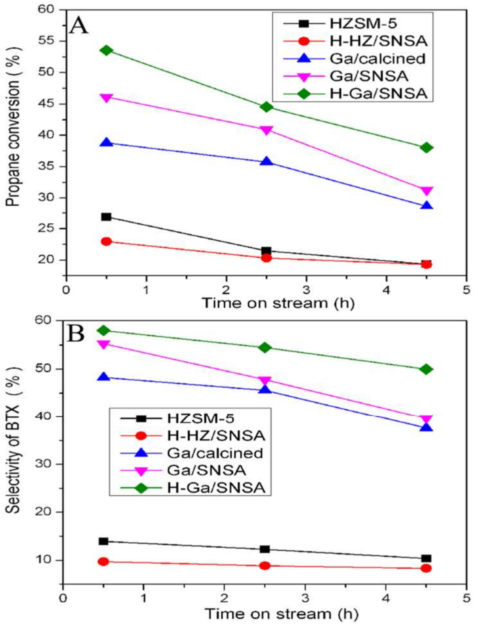

Fig. 1 Propane conversion (**A**) and selectivity of BTX (**B**) as a function of time on stream for as-prepared catalysts. Reaction conditions: P = 100 kPa, T = 540 °C, WHSV = 6000 ml/(g·h) and N_2/C_3H_8 molar ratio = 2.

In addition, the stability of H-Ga/SNSA is also investigated in comparison with that of Ga/calcined during two cycles of 900 min time-on-stream (Fig. S1). The results (Fig. S1A) reveal that H-Ga/SNSA and Ga/calcined both show gradual deactivation behavior under the conditions of large space velocity as a function of time on stream, but H-Ga/SNSA prepared using our proposed novel method shows much better catalytic performance than Ga/calcined prepared using conventional impregnation method always during the whole test period. On the other hand, from the test results of regenerated catalysts in Fig. S1B, it can be observed that activities of H-Ga/SNSA and Ga/calcined can be recovered substantially through a thermo-treatment to remove coke deposition at 540 °C in air. Meanwhile, stability patterns of H-Ga/SNSA and Ga/calcined are similar to those before regeneration as a function of time on stream. Furthermore, the propane conversion and selectivity of BTX over H-Ga/SNSA are still higher than those on Ga/calcined for the whole reaction time. The results of the durability and regeneration tests suggest that the catalyst crystals are reasonably stable under the conditions of the aromatization reaction.

3.2 Catalyst characterization

3.2.1 Catalyst composition and textural properties

Previous researches[21, 28-31] show that the XPS technique is certainly effective for charactering the situation on the surface of catalysts. Chemical states and the quantity of the elements that

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are present within the top 1-12 nm of the sample surface can be obtained by this technique. The bulk and surface compositions of the as-prepared catalysts are listed in Table. 1. As observed, comparison between ICP-AES and XPS data for Ga modified HZSM-5 zeolites shows surface of these catalysts are enriched in aluminum according to the smaller Si/Al ratios measured by XPS than the bulk Si/Al ratios determined by ICP-AES. After pre-treatment to HZSM-5 (impregnated with the bear gallium nitrate aqueous solution with and without formic acid, respectively), the surface aluminium content of the resulting Ga/dried and H-Ga/dried samples are higher than that of untreated HZSM-5 according to the surface Si/Al ratios, surface Al mol%, Al_{Td}/Al_{Oh} ratios and Al_{Oh}% (Td: four-coordinate framework Al and Oh: octahedral extra framework ^{27}Al as shown in Fig. S2). The spectra indicate that the framework of the precursor suffers from dealumination, especially for the sample impregnated by both gallium nitrate and formic acid, the dealumination is very severe. As for the samples after *in-situ* treatment such as Ga/SNSA and H-Ga/SNSA, their surface aluminium contents are higher than that of Ga/dried and H-Ga/dried, respectively. The results suggest that a second dealumination of the framework occurs during the *in-situ* treatment. Compared with that of Ga/dried, a lower surface aluminium content of Ga/calcined indicates that a portion of the surface aluminium species of Ga/calcined re-insert into the intracrystalline region. The H-Ga/SNSA zeolite undergoes the second dealumination perhaps because of the presence of steam[17] generated by self-decomposition of surface Ga (and other) species—inferred from Fig.S3. In addition, it can be seen that surface Si/Al ratios of the catalysts are lower than that of its bulk. It is probable that the partial surface Ga species could transport into the zeolite intracrystalline region. Surface Si/Ga ratios of H-Ga/SNSA and Ga/SNSA are higher than those of H-Ga/dried and Ga/dried respectively, which indicates that the *in-situ* treatment step is in favour of promoting the surface Ga into the intracrystalline region/channels of zeolites. However, the surface Si/Ga ratio of Ga/calcined is almost equal to that of Ga/dried. This implies that calcination under air greatly hinders the insertion of Ga into the intracrystalline region/channels of zeolite. To some extent, distinctions among the catalysts with regard to the quantity of elements can be distinguished obviously by the results of XPS at the same test conditions based on the same kind of materials. Furthermore, the gallium-to-framework aluminium ratio (Ga/Al_{FM}) of the Ga modified zeolites, measured by ICP-AES (Ga) and NMR spectroscopy (Al_{FM}), can be used to judge the dispersion of the Ga species, because it's positively related to the dispersion of the Ga species.[32] The ratios decrease in the following order for the three catalysts: H-Ga/SNSA (0.160) > Ga/SNSA (0.154) > Ga/calcined (0.150). It is inferred that the H-Ga/SNSA catalyst holds a higher degree of Ga dispersion over that of the other catalysts suggesting that this simple method has promise for catalytic applications.

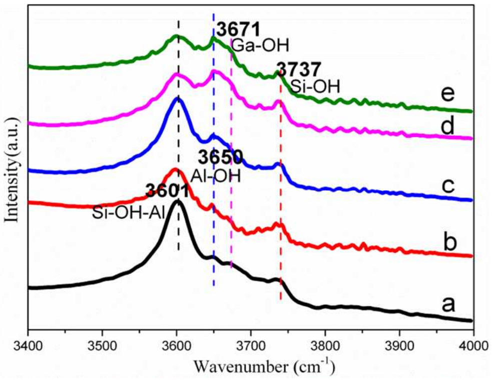

Fig. 2 DRIFT spectra in the OH stretching region of as-prepared ZSM-5 zeolites. (a) HZSM-5; (b) H-HZ/SNSA (c) Ga/calcined; (d) Ga/SNSA; (e) H-Ga/SNSA.

Table. 2 reports the textural properties of the as-prepared catalysts. One can observe that the micropore surface area and micropore volumes for the Ga modified ZSM-5 zeolites uniformly decrease in comparison with that for pure ZSM-5. Understandably, the decrease is because of pore blockage resulted from the dealumination and incorporation of Ga.[32] In addition, no significant changes are observed in the surface area and pore volume in the meso- and macropores regions. Based on the results of catalyst testing, it is plausible that the textural properties of the catalysts do not correlate with their catalytic activity. This is consistent with the results of Rodrigues *et al.*[32]

Table 1 Bulk and surface compositions of as-prepared ZSM-5 zeolites.

	Si/Al ratio		Al mol% [b]	Al_{Td}/Al_{Oh} ratio [c]	Al_{Oh}% [c]	Si/Ga ratio	
Sample	Bulk[a]	Surface[b]	Surface			Bulk[a]	Surface[b]
HZSM-5	19.1	20.9	1.53	18.3	5.18	/	/
Ga/calcined	18.9	17.2	1.62	15.7	5.99	150	21.2
Ga/dried	18.8	16.9	1.69	14.6	6.39	152	20.1
Ga/SNSA	18.8	16.4	1.74	10.8	8.42	152	35.1
H-Ga/dried	19.1	14.7	1.92	11.1	8.24	149	11.5
H-Ga/SNSA	19.1	10.9	3.67	8.51	10.5	149	18.9

[a] determined by ICP-AES method; [b] determined by XPS; [c] determined by ^{27}Al MAS NMR..

Table 2 Physical parameters of different as-prepared ZSM-5 zeolites

Sample	S^a_{BET} (m^2/g)	S^a_{micro} (m^2/g)	S_{ext} (m^2/g)	V^b_{total} (m^2/g)	V^b_{micro} (m^2/g)	V_{ext} (m^2/g)
HZSM-5	420	324	95.8	0.185	0.129	0.056
Ga/calcined	400	301	99.1	0.180	0.121	0.059
Ga/SNSA	397	298	99.1	0.178	0.119	0.059
H-Ga/SNSA	367	267	99.2	0.167	0.108	0.059

[a] determined by t-method; [b] determined by Volume adsorbed at p/p^0=0.97.

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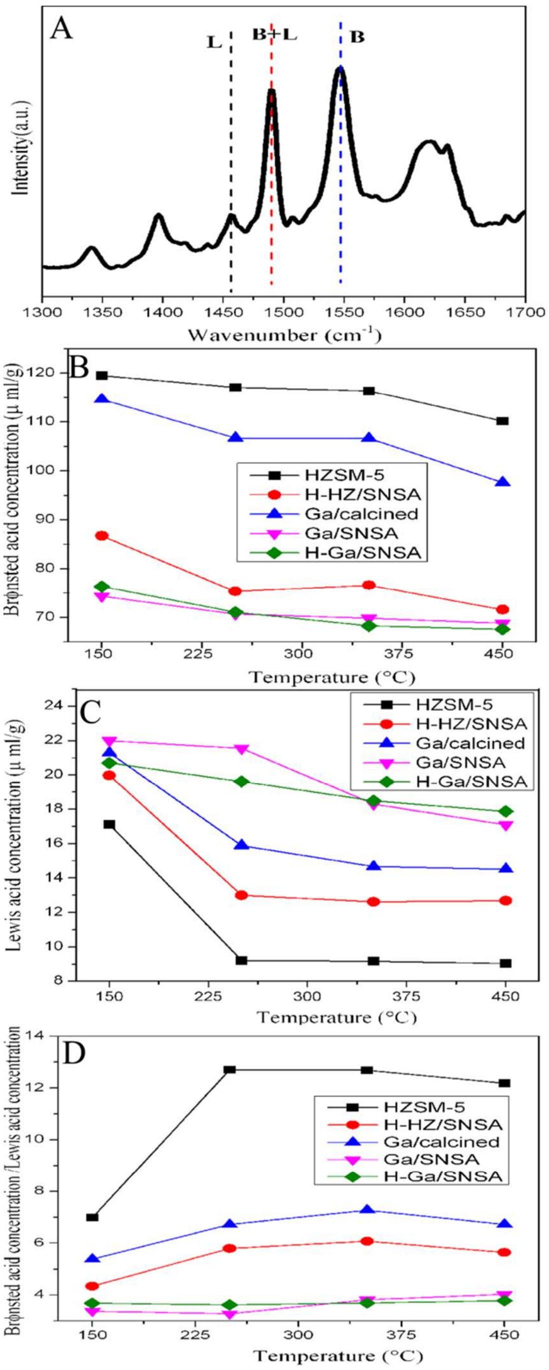

Fig. 3 The FTIR spectra of the pyridine adsorption on the catalysts and the quantified results of different acid sites. (A) Spectrum of HZSM-5 after evacuation at 450 °C; (B) Brønsted acid site concentration of samples at different temperatures; (C) Lewis acid site concentration of samples at different temperatures; (D) Brønsted acid site concentration/Lewis acid site concentration ratios of samples at different temperatures.

3.2.2 DRIFT and Pyridine-adsorption FTIR.

The infrared spectra in the OH stretching region for the catalysts are shown in Fig. 2. In this region, the peak at 3601 cm^{-1} is ascribed to the stretching vibration of Si(OH)Al bridged bonds, which are associated with the zeolite Brønsted acid sites.[25] By comparing the Ga/calcined material with HZSM-5, a reduction in the intensity of this peak can be observed with Ga incorporation analogous to that of H-Ga/SNSA compared with H-HZ/SNSA. The spectra suggest that the number of Brønsted acid sites decreases because of the exchange of acidic protons (Brønsted acid sites) with Ga species.[33] Another important feature is that the intensity of the peak centred close to 3650 cm^{-1}, which is usually associated with extra-framework aluminium OH species,[25] is enhanced with incorporation of Ga, indicating that the dealumination has occurred as previously described, which has been verified from the results of solid-state NMR and XPS in Table. 1. In addition, the intensity of the peak ~3671 cm^{-1} also increases, implying that the extra-framework gallium OH species are formed with quantitative incorporation of Ga, accordingly.

The FTIR spectra of the pyridine adsorption on the catalysts and the quantified results of different acid sites are shown in Fig. 3. The 1540 and 1450 cm^{-1} bands are attributed to pyridine adsorption on Brønsted acid sites and Lewis acid sites, respectively. As for the 1490 cm^{-1} band, it is believed to be a co-contribution of pyridine adsorption on the Lewis sites as well as on Brønsted acid sites (as shown in Fig. 3A).[32] In this work, the peaks ~1450 and 1540 cm^{-1} are used to quantify separately the Lewis and Brønsted acid sites. From Fig. 3B, it is clearly observed that the amount of Brønsted sites declines as a function of increasing evacuation treatment temperature for all samples. The introduction of Ga to materials such as Ga/calcined and H-Ga/SNSA leads to a modest decline in the number of Brønsted acid sites. Yet the decline in Brønsted acid sites is greatly deteriorated when those intermediate precursors were impregnated with formic acid followed by *in-situ* treatment. The data agrees with the previously shown infrared results in the OH stretching region. Fig. 3C shows pyridine adsorbed on Lewis acid sites. The observation is that Lewis acid sites of HZSM-5 and H-HZ/SNSA are almost completely removed after evacuation at 250 °C. However, as for other samples, especially H-Ga/SNSA, pyridine absorption is still present even at temperatures as high as 450 °C, indicating that stronger Lewis acid sites than originally present in the zeolite appear as a result of Ga incorporation via formic acid impregnation and *in-situ* treatment. Already published work [32,34-37] studying Zn and Ga modified zeolites, also concluded that the Brønsted acid sites were replaced by strong Lewis acid sites after Zn or Ga incorporation, and the strong Lewis acid sites associated with Ga modified ZSM-5 zeolites were related to highly dispersed Ga species. According to previous test results, the Ga/SNSA and H-Ga/SNSA materials have good catalytic activity. However, these two catalysts show the lowest ratio of Brønsted acid site/Lewis acid site as shown in Fig. 3D. Therefore it is feasible that tuning the ratio of Brønsted acid site/Lewis acid site has a significant effect on catalytic activity of propane aromatization, that is, the synergies between Brønsted acid sites and Lewis acid sites have a significant and direct impact on propane aromatization.

3.2.3 NH_3-TPD.

The distribution of acidity on as-prepared catalysts was measured by NH_3-TPD and the results shown in Fig. 4. All catalysts show two desorption peaks of NH_3 centred at 150–340 °C and 360–590 °C, which are associated with weak acid sites and strong acid sites, respectively. The desorption peaks of the Ga modified samples at 150–340 °C show reduced intensity than that of ZSM-5. However, the intensity of the desorption peak of H-HZ/SNSA at 360–590 °C dramatically declines, which implies that the sites associated with strong acidity are no longer present. This mainly results from zeolite dealumination via formic acid impregnation. The desorption peaks of Ga/calcined ascribed to the strong acid sites slightly decreases, however, the peak position shifts to higher temperatures (~500 °C), indicating that the acidic strength can be enhanced as a function of Ga incorporation. As for Ga/SNSA and H-Ga/SNSA, the peak area at 360–590 °C is almost identical with both materials displaying a higher degree of reduction than that of the other three catalysts. It is plausible that the *in-situ* treatment to (H-)Ga/dried precursor leads to a decline in the numbers of acid sites because of the exchange of acidic protons (Brønsted acid sites) with ionic gallium species entering into zeolite intracrystalline region/ channels.

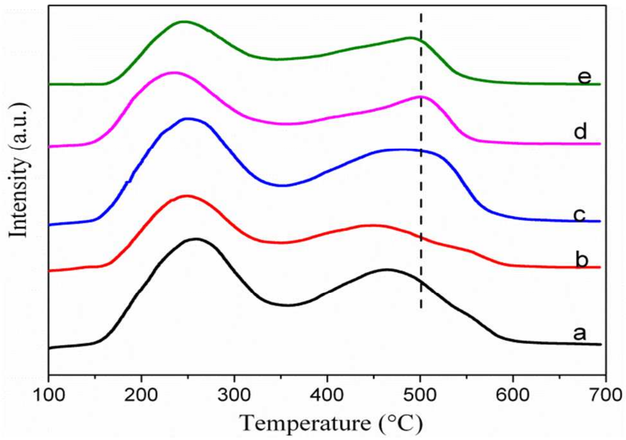

Fig.4 NH_3-TPD profiles of different as-prepared ZSM-5 zeolites. (a) HZSM-5; (b) H-HZ/SNSA (c) Ga/calcined; (d) Ga/SNSA; (e) H-Ga/SNSA.

3.2.4 H_2-TPR.

H_2-TPR profiles of the as-prepared samples are displayed in Fig. 5. Pure Ga_2O_3 exhibits two reduction peaks, centred close to 507 °C and 771 °C (in Fig. 5), which are ascribed to small Ga_2O_3 particles and segregated bulk Ga_2O_3, respectively.[21] Upon Ga introduction to the ZSM-5 zeolite, the reduction becomes difficult, and as such the two reduction peaks of the Ga modified ZSM-5 catalysts translate to higher temperatures (centred ~528-533 °C and 810-839 °C) as observed in curves b, c and d, Fig. 5. The principal reason in the increase of the reduction temperature is related to the Ga_2O_3 species being highly dispersed on the ZSM-5 zeolite host. Besides, an additional, and new reduction peak centred at ~648-671 °C for the Ga modified ZSM-5 catalysts is present. Previous literature[18, 23, 24, 38] has reported the strong interaction between highly dispersed Ga species and ZSM-5 zeolite produced $(GaO)^+$(III) species, while the $(GaO)^+$(III) species could be further reduced to Ga^+(I). The peak associated with the reduction from $(GaO)^+$(III) to Ga^+(I) corresponds to the peak at 648-671 °C. Through fitting of the TPR profiles and calculating their peak areas, the data suggests the $(GaO)^+$ content of H-Ga/SNSA is higher than that of the Ga/calcined and Ga/SNSA (Table S1).

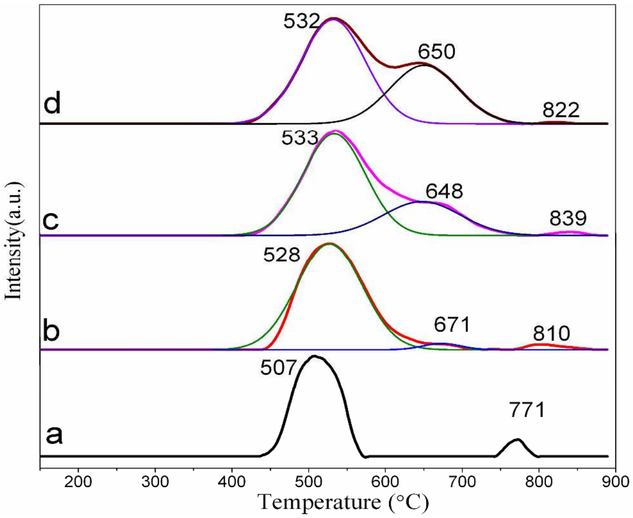

Fig. 5 H_2-TPR profiles of different samples. (a) Ga_2O_3; (b)Ga/calcined; (c)Ga/SNSA;(d) H-Ga/ SNSA

3.2.5 XPS.

The characterization of XPS is effective for chemical states of the elements on the surface of the zeolites. Already published work[21, 25, 39, 40] has reported that XPS technique is used to characterize the states of Ga in non-framework or extra-framework positions on the surface of the catalysts. Fig.6 shows Ga $2p_{3/2}$ XPS spectra of the as-prepared catalysts. It can be observed that the Ga $2p_{3/2}$ binding energy value (BEs) for Ga/calcined (1119.1 eV) is higher than that for Ga_2O_3 (1117.9 eV), indicating that a strong interaction between the ionized Ga species and ZSM-5 zeolite, while the Ga $2p_{3/2}$ BEs for the H-Ga/SNSA (1118.7 eV) is lower than that for Ga/calcined. This decrease of BEs for Ga/SNSA is related to the strong covalent bonding character between the surface highly dispersed Ga species $(GaO)^+$ and the framework of the ZSM-5 zeolite according to Izabela Nowak *et al.*[21] The XPS

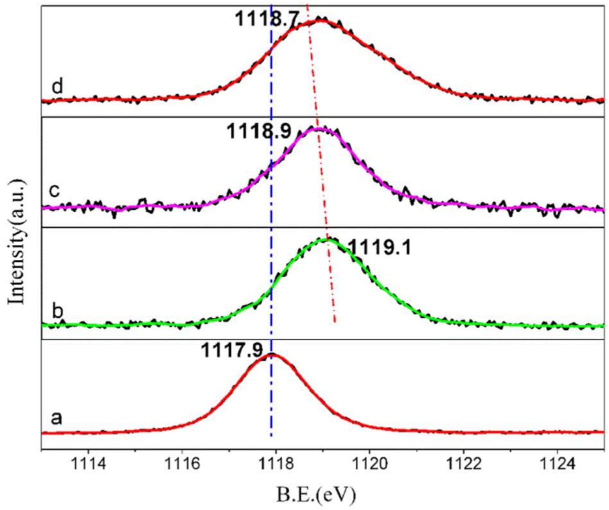

Fig. 6 Ga $2p_{3/2}$ XPS spectra of different samples. (a) Ga_2O_3; (b) Ga/calcined; (c) Ga/SNSA; (d) H-Ga/SNSA.

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data suggests that this novel treatment method is favourable for the formation of $(GaO)^+$ species. It has been proved that highly dispersed $(GaO)^+$ species which exchange with acidic protons (Brønsted acid sites) of the zeolite framework presented as Si-O($(GaO)^+$)-Al in extra-framework positions on the surface of the catalysts, contribute to strong Lewis acidity[32], concordant with the Py-FTIR results that there are greater numbers of strong Lewis acid sites on the H-Ga/SNSA material.

3.3 Discussion

According to previous literature[1, 25] and the results reported herein, the dispersion and state of the Ga species within the catalyst strongly dictated their activity to propane aromatization. The addition of trivalent Ga^{3+} ions into ZSM-5 using conventional impregnation methods is quite difficult because of the highly positive electrostatic charge and the bulky size of $[Ga(H_2O)_6]^{3+}$ aquacomplexes,[41] and thus Ga^{3+} ions tend to reside predominantly on the external surface of zeolite as single extracrystalline Ga_2O_3. Hence, prepared catalysts by this methodology display suboptimal activity. However, in the case of our prepared H-Ga/SNSA catalyst, the Ga component $(GaO)^+$) was found to be well dispersed within the zeolite intracrystalline region/channels via formic acid impregnation and *in-situ* treatment method is remarkably generic to allow preparation of highly active catalysts for propane aromatization. As reported,[26] the $Ga(OH)_x^{y+}$ ($x = 1, 2; y = 3 - x$) species can be produced in an acid environment. In our experiment, an abundance of $Ga(OH)_x^{y+}$ species are accordingly formed on catalyst surface because of the presence of formic acid. The formed precursor species were prone to move into the zeolite channels and interact with framework protons (Si(OH)Al) of the ZSM-5. Finally, the linkage between Ga and ZSM-5 is favourable for subsequent treatment procedures to prepare highly dispersed and active Ga modified catalysts. In addition, it is reported that the pH value of the solution during impregnation affects the dispersion of Ga species.[25] Therefore, the quantity and nature of the acid used certainly leads to different Ga dispersion. The samples prepared by treatment with different acids and their amount, for example, with formic acid (such as H(half)-Ga/SNSA and H(double)-Ga/SNSA), differ in their catalytic activities (shown in Fig. 7). The catalytic activities of H(half)-Ga/SNSA and H(double)-Ga/SNSA are lower than that of H-Ga/SNSA but remain higher than that of Ga/calcined. It suggests that an optimum acidity to the solution is required to optimize the catalyst properties, thereby leading to differences in activity. As for the catalysts impregnated by acetic acid, nitric acid and citric acid, improvements in their respective activities are significant together with their selectivity toward BTX and are similar to H-Ga/SNSA. The results indicate that the acidity of the solution plays a crucial role the observed activity, as each catalyst results in differing degrees of Ga dispersion.[25] On the other hand, one should not neglect that the acid treatment has a modest effect on the zeolite structure/morphology such as pore size, dealumination and acidity, etc. Although the increase of amount of formic acid is in favour for the formation of $Ga(OH)_x^{y+}$ precursors, such as $Ga(OH)_2^+$ and $Ga(OH)^{2+}$, the dealumanition and damage to the ZSM-5 framework are remarkably severe as well as the increased acid strength of nitrate acid solution.[42, 43] Because of near acid strength to formic acid, H(acetic)-Ga/SNSA shows slight change of activity. As for H(citric)-Ga/SNSA, the residues of citric acid can be only removed off through subsequent calcination process.[44] Here, zeolite texture is probably affected during calcination, thereby the activity of H(citric)-Ga/SNSA decreases. In the case of *in-situ* treatment, the above mentioned $Ga(OH)_x^{y+}$ species decomposed to $(GaO)^+$ under a static N_2 atmosphere at high temperature as Eq. (3).[32] At the same time, a significant quantity of steam was generated and maintained within the reactor. The

decomposition of the samples was monitored by TG-MS (Fig.S3).

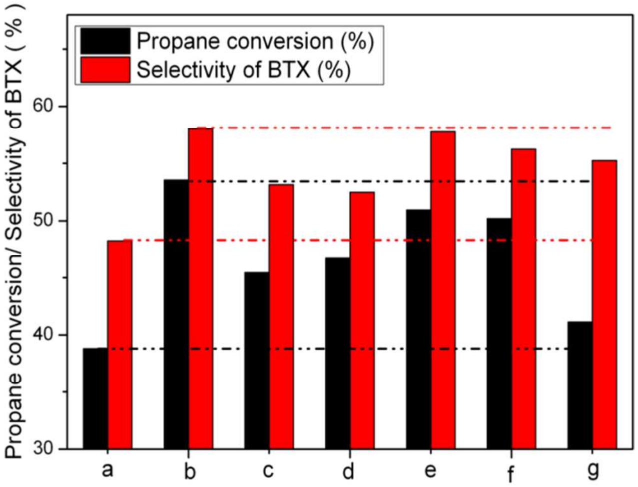
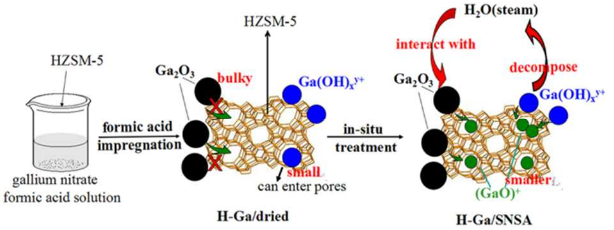


Fig. 7 Propane conversion and selectivity of BTX on as-prepared ZSM-5 zeolites. Reaction conditions: P = 100 kPa, T = 540 °C, WHSV = 6000 ml/(g·h), N_2/C_3H_8 molar ratio = 2, time on stream is 0.5h.(a) Ga/calcined; (b)H-Ga/SNSA;(c)H(half)-Ga/SNSA;(d)H(double)-a/SNSA;(e)H(acetic)-Ga/SNSA; (f) H(nitric)-Ga/SNSA;(g) H(citric)-Ga/SNSA.



Scheme 1 Probable mechanistic route of H-Ga/SNSA

$$Z{-}Ga(OH)_2^+ \rightarrow Z{-}GaO^+ + H_2O \qquad (3)$$

(Z^- represents an ion-exchange site at the zeolite framework) Ausavasukhi and Sooknoi[45, 46] reported that part of the bulk Ga_2O_3 of Ga/HZSM-5 (prepared by conventional impregnation methods) could be re-dispersed under the current steaming conditions, thereby forming GaO(OH), which can easily interact with protons from Brønsted acid sites and further convert to extra framework $(GaO)^+$ species (as show in Eq.(4)) and Eq. (5)).

$$Ga_2O_3 + H_2O \rightarrow 2GaO(OH) \qquad (4)$$

$$GaO(OH) + H_z^+(\text{Brønsted sites}) \rightarrow GaO^+ + H_2O \qquad (5)$$

In our experiment, $Ga(OH)_x^{y+}$ or $[Ga(H_2O)_6]^{3+}$ species, within the formic acid impregnated samples, under the experimental conditions, also should transform into extracrystalline Ga_2O_3 during the air drying at 120 °C for 8 h. Here, the extracrystalline Ga_2O_3 can be further converted into $(GaO)^+$ species under a steam environment. Based on the above, the novel formic acid impregnation and *in-situ* treatment method favors promoting the surface Ga into the intracrystalline region forming highly dispersed active $(GaO)^+$ species.

According to above, a probable mechanistic route for the H-Ga/SNSA catalyst can be deduced as scheme 1. Briefly speaking, in the process of formic acid impregnation, the $Ga(OH)_x^{y+}$ species are formed under the acidic environment. Subsequently, a portion of the $Ga(OH)_x^{y+}$ species are inevitably converted to extracrystalline Ga_2O_3 via drying, while the remainder moves into the ZSM-5 intracrystalline region, owing to their small size, and interacts with the framework of the ZSM-5 zeolites. When the resulting sample is subjected to the *in-situ* treatment, the undecomposed $Ga(OH)_x^{y+}$ species are further converted to $(GaO)^+$, accompanied by the by-product steam, wherein, the extracrystalline Ga_2O_3 also easily reacts with the steam, finally leading to the formation of highly active $(GaO)^+$ species in abundance.

Propane aromatization contains a series of processes: olefin formation through dehydrogenation of propane to propene, oligomerization of olefins, subsequent cracking (olefin interconversion), formation of new oligomers through olefin alkylation followed by a hydrogen transfer and/or dehydrogenation, and cyclization and aromatization.[47] Among them, the dehydrogenation of propane is one of most critical process of propane aromatization.[1] Generally, it is thought that the acidity of the metal-modified zeolite catalyst is quite an important and relevant factor affecting catalytic activity in heterogeneous catalysis reactions. In our present catalytic system, the highly dispersed $(GaO)^+$ species generate strong Lewis acid sites by interacting with acidic protons (Brønsted acid sites) of the zeolite framework, which are responsible for enhancing dehydrogenation, while the Brønsted acid sites on ZSM-5 contribute to the whole processes of propane aromatization. It is apparent that the strong Lewis acid sites generated by the $(GaO)^+$ species and Brønsted acid sites have a synergistic effect on propane aromatization. This can well explain why our prepared H-Ga/SNSA has excellent catalytic behaviour in relation to propane aromatization.

At this stage of the research, it could not be easily established as to how exactly the $(GaO)^+$ species present on the catalyst are converted to the reduced state species ($Z{-}Ga^+$) during aromatization as other literatures[17, 22, 25, 48-50] however, on at least one count, the $(GaO)^+$ species are quite a useful intermediate for propane aromatization. The work is still on-going.

4. Conclusion remarks

A novel preparation method containing formic acid impregnation and *in-situ* treatment was developed to prepare a highly active catalyst for propane aromatization. The prepared catalysts showed remarkably superior activity, and the propane conversion and selectivity of BTX on the H-Ga/SNSA catalyst achieved 53.6% and 58.0% respectively—significantly higher than that of catalyst prepared using traditional impregnation method (38.8% and 48.2%) when tested after 0.5 h on-stream. Furthermore, the activity of H-Ga/SNSA was shown to be constantly higher than that of Ga/calcined in an evaluation period of 4.5 h. Characterization results such as BET, XPS, H_2-TPR, etc. suggested that formic acid impregnation and *in-situ* treatment both made the ZSM-5 zeolites exposed to dealumination. Simultaneously, this novel treatment process enhanced the dispersion of gallium species and promoted the formation of highly dispersed $(GaO)^+$ species in the zeolite intracrystalline region through decomposition of intermediate species, such as $Ga(OH)_x^{y+}$ and the interaction between Ga_2O_3 and water (steam). $(GaO)^+$ species were shown to exchange acidic protons (Brønsted acid sites) of the zeolite framework and contributed to the strong Lewis acidity, which was favourable for propane dehydrogenation as well as the contribution of the Brønsted acid sites to the whole aromatization processes. It is apparent that the strong Lewis acid sites generated by the $(GaO)^+$ species and the Brønsted acid sites have a synergistic effect on propane aromatization.

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Notes and references

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Supplementary text; Fig.S1-S3; Table S1. See DOI: 10.1039/b000000x/

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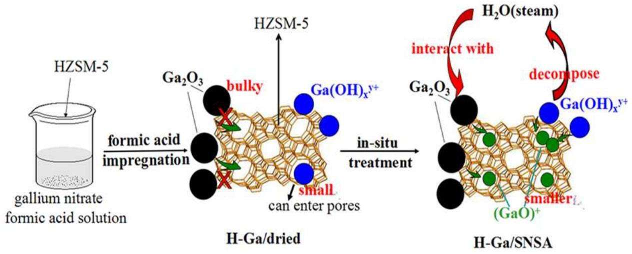

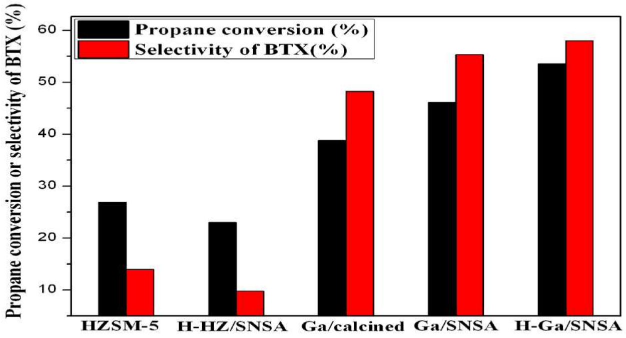

A highly efficient Ga/ZSM-5 catalyst prepared by formic acid impregnation and *in-situ* treatment shows remarkably superior activity for propane aromatization.