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Propane dehydrogenation (PDH) is one of the most promisng candidates of propylene production process to meet the growing demand of propylene in the future. There is an urgent need to develop catalysts for PDH. In this work, we have synthesized high silica Ga-Beta as a new candidate of the catalyst from dealuminated zeolite using dry gel conversion method. The high silica Ga-Beta wih Si/Ga ratio up to 177 can be synthesized. On the PDH reaction, synthesized Ga-Beta showed the highest propane conversion and the highest propylene yield in Ga-based zeolites. The combination of Ga species incorporated into zeolite frameworks, large microporosity and Brønsted acidity is likely to lead to the excellent catalytic peformance of the Ga-Beta. Moreover, the Ga-Beta with higher Si/Ga ratio shows longer catalyst lifetime on PDH reaction since coke deposition rate was depressed by the decrease of the acid amount. This work provides new insights for PDH reaction over Ga based zeolite catalysts, which would contribute to the progress in activation and transformation of light alkenes to value-added chemicals.

Introduction

Propylene is one of the most important materials for chemical production in petrochemical industry; e.g., polypropylene, acrylonitrile, propylene oxide, and oxy alcohols are mainly produced from propylene [1-9]. Propylene is mainly produced as one of by-products of steam cracking of naphtha to produce ethylene; however, it is difficult to increase the yield of propylene. Furthermore, steam cracking of naphtha has gradually been replaced with that of ethane to produce ethylene more effectively, and the latter hardly yields propylene; the shortage of propylene is anticipated. To meet the growing demand of propylene in the future, it is necessary to develop a process to produce propylene as the main product.

Propane dehydrogenation (PDH) process is the most promising candidate of the process because propylene can be directly and mainly produced using propane derived from abundant natural gas. Therefore, research efforts have focused on developing excellent catalysts for the PDH process. Catalysts based on Pt are well known to be highly effective for the PDH process. [4-8, 10-15] High propane conversion and propylene selectivity had been achieved on PDH reaction using mesoporous silica doped with Pt and Sn [4]. However, the cost disadvantage of precious metals like Pt keeps the catalysts based on them from practical applications. The representative catalyst based on non-precious metals for PDH process is a series of the zeolites modified with Zn or Ga ions [9, 15-17]. Zn species in zeolites is often reduced by H_2 produced in the PDH reaction and vaporized under high temperature reaction, and therefore, the stability of zeolites modified with Zn is lower than those modified with Ga. Meanwhile, gallosilicate MFI zeolites have a lower rate of deactivation and higher propylene selectivity than the other zeolites doped with non-precious metals [9]. But the performance of the zeolites modified with Ga is much poorer for PDH process than catalysts based on Pt.

To develop zeolite catalysts based on non-precious metals showing high catalytic performance for the PDH process, we should focus on the reaction pathways in zeolites. There are two pathways from propane to some chemicals in zeolites; the initial reaction step from propane is dehydrogenation to propylene or cracking to ethylene and methane, and then,

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aromatic compounds can be produced through the excessive reaction of the produced propylene or ethylene and methane as shown in Fig. 1 [18-21]. To use zeolites for the PDH process, we should inhibit the cracking reaction and the excessive reactions in the present zeolites. The Ga species incorporated in zeolite frameworks as active sites for PDH process has Brønsted acidity important for propylene selectivity at the initial step. Meanwhile, excess Brønsted acid sites promote excessive reactions to result in coke formation; it causes low selectivity of desired products and rapid deactivation. To inhibit the excessive reactions, high silica zeolites are preferable. In addition to that, the pore size and pore structure of zeolite are important. Zeolite Beta, which is *BEA type zeolites, has a three-dimensional porous network including 12-membered rings (12-MRs). Generally, larger micropores improve mass transfer. The micropores of zeolite Beta are larger than widely used other structures like MFI and CHA structures with 10-MRs and 8-MRs, respectively. The increase of diffusibility can result in the improvement of propane conversion and propylene selectivity. In addition, hierarchical pore structured Ga-MFI materials exhibit superior propane conversion efficiency and propylene selectivity to bulk Ga-MFI materials for the PDH process [17].

These findings imply that high silica zeolite Beta with Ga (Ga-Beta) should be an ideal catalyst for the PDH process. Although normal methods are not applicable to synthesize high silica Ga-Beta, dry gel conversion (DGC) methods could be applicable. So far, unique zeolites have been synthesized by DGC method; e.g. nano-sized SAPO-34 [22], nano-sized Fe-MFI [23], and Ge incorporated aluminophosphate zeolite [24]. Recently, we have reported high silica zeolite Beta with Fe (Fe-Beta) can be synthesized by the DGC method using dealuminated Beta as one of the ingredients [25]. In this synthesis, it was impossible to synthesize Fe-Beta without dealuminated Beta. Herein, we report the synthesis of high silica Ga-Beta by applying the modified DGC method. Moreover, we discuss the effects of acidity, the crystal structures and the oxidation states of Ga species on the PDH reaction. The structures of the obtained samples are clarified by X-ray diffraction (XRD), nuclear magnetic resonance (NMR) spectroscopy and X-ray fluorescence (XRF) analysis, and the acidic properties are evaluated by NH_3 temperature programmed deposition (NH_3-TPD) and Infrared (IR) spectroscopy by of adsorbed CD_3CN.

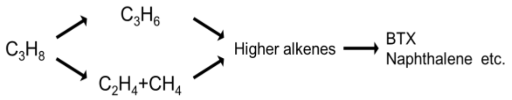

Fig. 1 PDH reaction scheme.

Experimental

The dealuminated Beta zeolite (deAl-Beta) was prepared using commercially available Al-Beta (SiO_2/Al_2O_3=28.9, Tosoh Co. Ltd.) referring to our previous work [24]. Gallium nitrate, $Ga(NO_3)_3.nH_2O$ (Wako Pure Chemical) and 40 wt% colloidal silica (CS, Aldrich) were used as Ga and Si sources, respectively. Tetraethylammonium hydroxide (TEAOH) working as organic structure-directing agent (OSDA) was used in the form of a 35 wt% aqueous solution (Aldrich). The molar ratios of the precursor solution were 5 SiO_2 (CS): 5 SiO_2 (deAl-Beta): x Ga_2O_3 : 2.5 TEAOH : 0.33 NaOH : 100 H_2O (x=0.033, 0.025, 0.0167). The precursor solutions were stirred at room temperature for 2 h, and then, the solvents were evaporated. The obtained dry gel was crystallized at 393 K for 72 h under steam. To remove the OSDA, the calcination under air was performed at 823 K for 5 h. Obtained sample was named Na/Ga-Beta. We used 0.1 mol/L aqueous ammonium nitrate solutions to exchange the cation from Na^+ into NH_4^+. Then, calcination was performed at 823 K for 5 h to obtain the H^+ type sample. The sample was donated as 'Ga-Beta'.

In addition, we also prepared Ga loaded deAl-Beta by impregnation to investigate the state of Ga species on catalytic performance. The detailed procedures are shown below. The obtained deAl-Beta (1.0 g) was suspended in 100 g of 1.7 mmol/L aqueous solution of $Ga(NO_3)_3$. After stirring at 343 K for 24 h, washing with deionized water and drying at 363 K, the obtained powder was calcined at 823 K for 5 h to give Ga/deAl-Beta.

The crystal structures of all products were determined XRD patterns recorded on the PANalytical X'Pert-MPD diffractometer using Cu-Kα radiation. The ^{71}Ga MAS NMR spectrum was recorded at ambient temperature by using 4 mm diameter zirconia rotors spinning at 14 kHz on a ECA-500 NMR (JEOL Ltd.) to evaluate the amount of Ga species. NH_3-TPD was measured by using BEL CAT II and BEL mass (MicrotracBEL). IR spectra were collected on Nicolet 380 (Thermo Fisher Scientific) with a MCT detector by averaging 100 scans at 43 cm-1 resolution in the 4000 to 400 cm-1 range. Before the IR measurement, samples were treated in a vacuum at 723 K for 4 h. CD_3CN (Tokyo Chemical Industry) was adsorbed at 393 K for 1 h and evacuated at 423 K.

PDH reaction over zeolite catalysts was carried out using a fixed-bed reactor made of quartz glass (i.d. 4 mm) with a continuous–flow system under atmospheric pressure at 923 K. The composition of feed gas was 10 mol % C_3H_8/ 90 % He and the gas was introduced at 10.2 mL/min (Ga-Beta-150, Al-Beta, Ga-MFI-150, Ga/deAl-Beta and Na/Ga-Beta) or 6.69 mL/min (Ga-Beta-200, Ga-MFI-200, Ga/deAl-Beta-200). . The products were analysed online with Shimadzu GC-2025 and GC-2014 gas chromatographs equipped with a flame ionization detector. The propane conversion and the yields of products were calculated according to following equation:

$$C = \left(1 - \frac{R_f}{R_0}\right) \times 100, \qquad (1)$$

$$Y = \frac{P}{R_0} \times 100, \qquad (2)$$

where C denotes propane conversion [C-mol%], R_0 denotes initial amount of propane, R_f denotes amount of propane after reaction, Y denotes product yield and P denotes amount of product. The coke contents of the catalysts were determined in a thermogravimetric analyser (TGA). The weight loss observed from 573 to 973 K was ascribed to coke.

Results and discussion

We applied the DGC method using dealuminated zeolite to synthesize the high silica Ga-Beta zeolite (See Experimental) [25]. The obtained Ga-Beta zeolites were named Ga-Beta-150, Ga-Beta-200 and Ga-Beta-300 corresponding to their initial Si/Ga ratio, 150, 200 and 300, respectively. XRD patterns for the Ga-Beta samples prepared using the precursors with different Si/Ga ratios show peaks derived from *BEA structure at 8 and 23 degree as shown in Fig. 2. Since there are no other peaks, Ga-Beta zeolites do not contain any crystalline byproducts like gallium oxide and any aggregated Ga species. In addition, any peaks derived from amorphous species are not detected. However, we cannot know if prepared samples contain Ga species using only XRD. According to SEM images as shown in Fig. S1 (see Supprimentary Information), it is revealed that Ga-Beta-150 and -200 have almost same morphology.

For comparison with Ga-Beta, we synthesized Ga/deAl-Beta from dealuminated Beta zeolite (See Experimental). We named Ga/deAl-Beta-100 and Ga/deAl-Beta-200 according to initial Si/Ga ratios, Ga/deAl-Beta-100 and Ga/deAl-Beta-200. XRF measurement was carried out to know actual Si/Ga ratios in the Ga-Beta and Ga/deAl-Beta samples. XRF measurements indicate that all samples contained Ga species as shown in Table 1. However, Si/Ga ratios of Ga-Beta sample were smaller than those in the starting precursors, implying Si species was slightly dissolved and lost during washing. Such a phenomenon often occurs in the synthetic processes of high silica zeolites [26]. Ga-Beta-300 shows exceptionally low Si/Ga ratios. The maximum Si/Ga ratio of the obtained Ga-Beta is 177, and this value is still high enough for this study. We should clarify the states of Ga species in the obtained zeolites using other measurements.

Table 1 Si/Ga ratio of Ga-Beta and Ga/deAl-Beta.

Sample	Si/Ga [-]
Ga-Beta-150	121.2
Ga-Beta-200	177.7
Ga-Beta-300	127.8
Ga/deAl-Beta-100	114.1
Ga/deAl-Beta-200	157.9

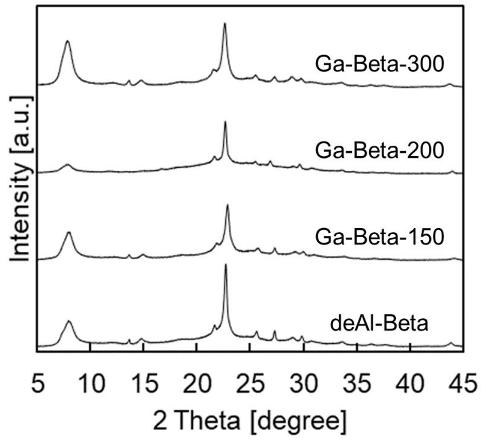

Fig. 2 XRD patterns of the synthesized Ga-Beta samples and the deAl-Beta as the ingredient.

The amounts of the acid sites in the obtained zeolites can be estimated by NH_3-TPD measurement. The NH_3-TPD profiles of the Ga-Beta zeolites show a peak derived from Brønsted acid sites as shown in Fig. 3 (a). These results indicate that Ga species is well incorporated into the framework of *BEA structure and works as acid sites. In addition, the peak intensity of the NH_3-TPD profile, which corresponds to the amount of acid sites, for Ga-Beta-200 is smaller than that for Ga-Beta-150. These results are consistent with the XRF analysis and imply the possibility of the Ga-Beta to work as acid catalysts for PDH reaction.

The results of the NH_3-TPD measurements for the other zeolites were shown as Fig. 3 (b). Na/Ga-Beta (See Experimental) shows no peaks derived from Brønsted acid sites; almost all counter cations are Na^+ ions instead of Brønsted acidity. Furthermore, Ga/deAl-Beta sample also show no peaks. It suggests that Ga species is not incorporated into the framework, and the crystallization process by DGC method in the presence of OSDA is required to incorporate Ga species into the zeolite framework. In addition, we measured CD_3CN IR spectra (Fig, 4). This result also clarifies that Ga-Beta-200 has Brønsted acid sites while Ga/deAl-Beta and Na/Ga-Beta does not.

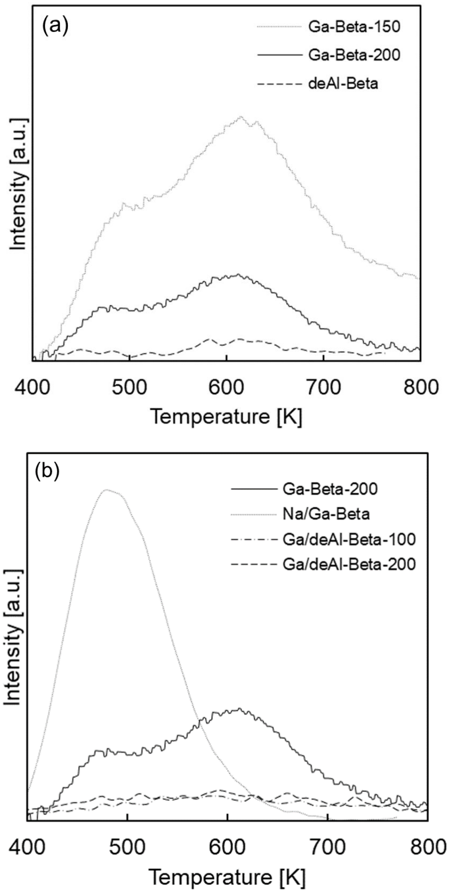

Fig. 3 NH_3-TPD profiles of (a) Ga-Beta and deAl-Beta and (b) Ga/deAl-Beta, Na/Ga-Beta and Ga-Beta.

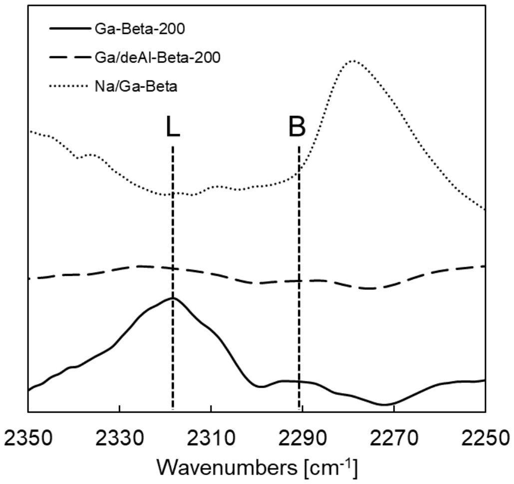

Fig. 4 CD_3CN spectra of Ga-Beta-200, Ga/deAl-Beta-200 and Na/Ga-Beta.

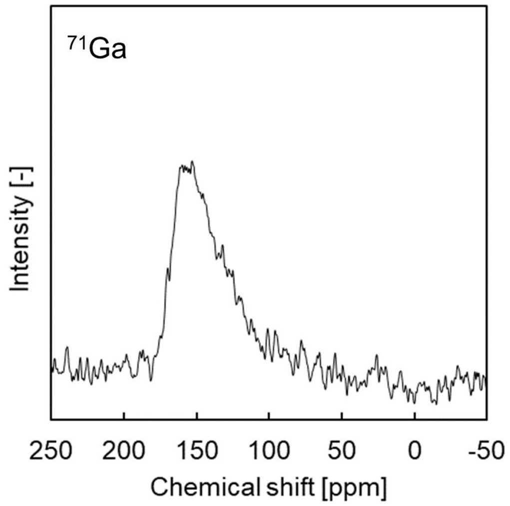

Fig. 5 ^{71}Ga NMR spectrum of Ga-Beta-150.

We measured NMR spectra to decide the Ga species in the obtained Ga-Beta zeolites. A ^{71}Ga NMR spectrum for Ga-Beta-150 exhibits a signal derived from Ga^{3+} species with tetrahedral framework at 150-160 ppm, whereas it does not show any peaks derived from extra-framework Ga species around 50 ppm [27-29]. These imply that Ga species is well incorporated into the framework for the Ga-Beta samples. Meanwhile, the spectrum for Ga-Beta-200 shows no peaks; the amount of Ga species is likely to be too small. This result should be confirmed by the amount of acid sites.

The value X represents the ratio of two reaction routes (propylene/ (methane + ethylene)). As expected, Ga-Beta catalysts showed the highest propane conversion and propylene yield. We compare the Ga-Beta catalysts with various zeolite catalysts in detail to find the factors that affect the catalytic activity.

The X value of Ga-Beta-200 is higher than Ga-Beta-150 in spite of almost the same conversion value as Ga-Beta-150; the decrease of acid sites leads to the increase of the selectivity of the hydrogenation route. The low X value and relatively high propane conversion for the PDH process with Al-Beta indicates that Al species promotes cracking reaction much more than dehydrogenation. The low values of conversion and X with both Ga-MFI indicate that smaller micropores decrease diffusibility and prevent propane from being converted and selecting the dehydrogenation route. Both of the Ga-deAl-Beta

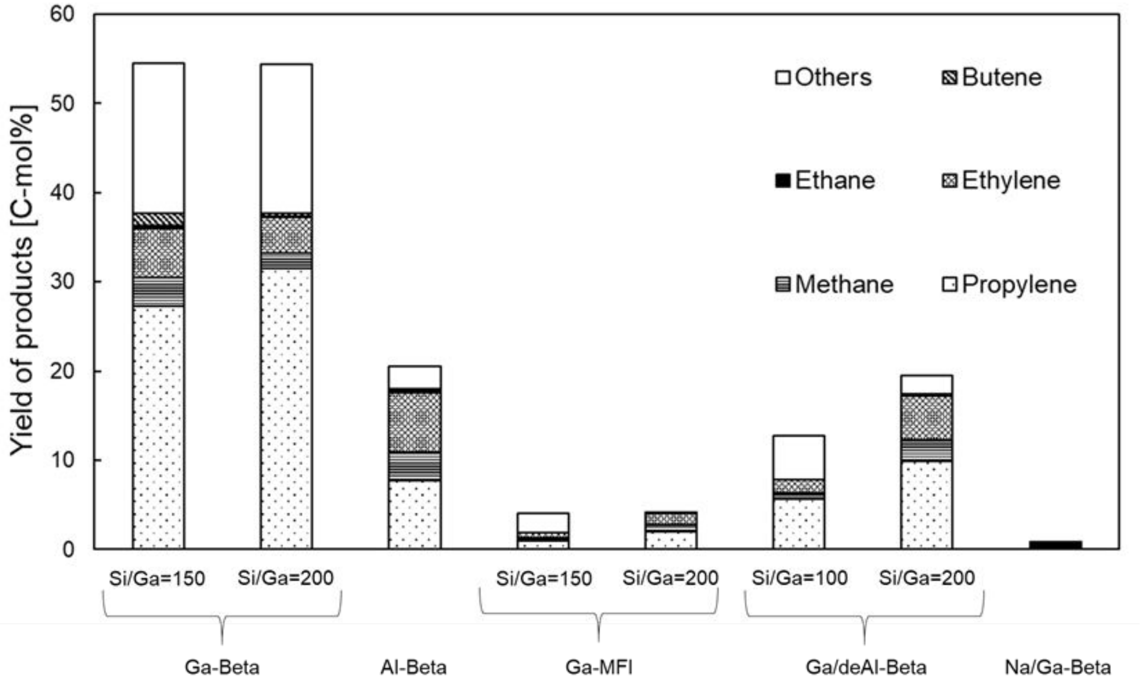

Fig. 6 Product distribution of PDH reactions over zeolite catalysts after 15 min.

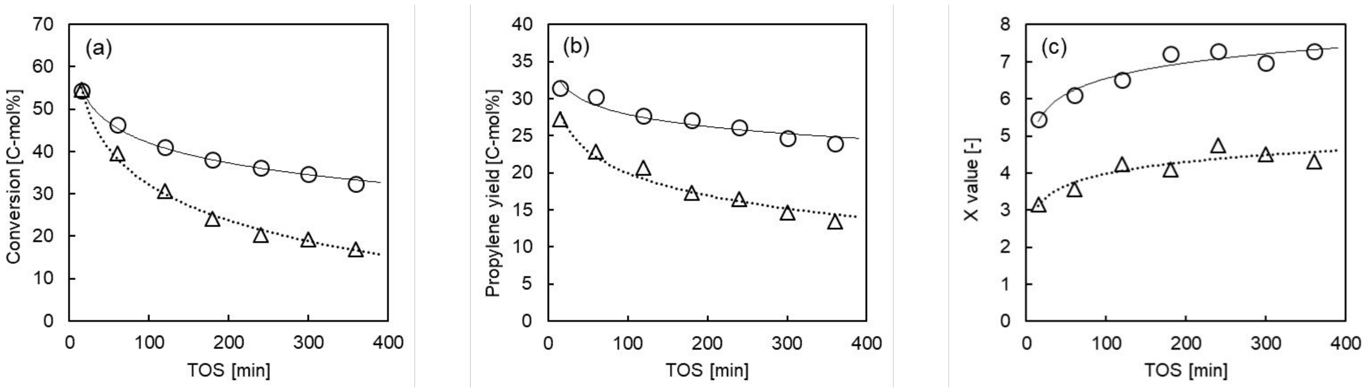

Fig. 7 Change of (a) propane conversion, (b) propylene yield and (c) X value of PDH reaction with time on stream over Ga-Beta-150 (Δ) and Ga-Beta-200 (O).

samples are inferior to Ga-Beta catalysts. The comparison of conversion and X of both of them implies that it is difficult to improve both conversion and X simultaneously. These results indicate that the incorporation of Ga species into the zeolite framework is crucial to the catalytic performance. Over all catalysts except Na/Ga-Beta, ethylene yield is almost twice as much as methane yield. This result follows a theory and suggests the validity of the cracking route.

The inertness of Na/Ga-Beta catalyst without Brønsted acidity indicates that acid sites are required to convert propane.

To evaluate the deactivation process of Ga-Beta zeolites, the time courses of propane conversion, propylene yield and X value were measured as shown in Fig. 7. Propane conversion and propylene yield of Ga-Beta-150 considerably decreased for 6 h. Meanwhile, Ga-Beta-200 maintained high performance for 6 h. This is clearly due to the difference of the amount of acid sites. The decrease of acid sites could result in the suppression of undesirable excessive reaction and coke deposition. Ga-Beta-200 has mesoporosity according to its N_2 adsorption isomer as shown in Fig. S2 (see Supprimentary Information). The mesoporosity may improve the diffusivity of reactants and products, which may result in the suppression of undesirable excessive reaction and coke deposition. The amounts of coke on each catalyst were also measured as shown in Table 3. Although reaction time was longer for Ga- Beta-200 than for Ga-Beta-150, the amount of coke was much smaller. It indicates that the higher the Si/Ga ratio is favorable for not only the higher selectivity of dehydration route but also the longer the lifetime of catalyst is. In addition, the mesoporosity of Ga-Beta-200 would be also favorable for the longer lifetime of catalyst. These results suggest that the combination of Brønsted acidity, Ga species incorporated high Si/Ga ratio and large microporosity is very important for catalytic performance.

Table 2 Numerical value of conversion, yield of propylene, methane and ethylene, and X.

Catalysts	Converion [C-mol%]	Product Yield [-]			X value [-]
		C3=	C1	C2=	
Ga-Beta-150	54.5	27.3	3.2	5.5	3.1
Ga-Beta-200	54.3	31.5	1.8	4.0	5.4
Al-Beta	20.6	7.7	3.2	6.7	0.8
Ga-MFI-150	4.0	1.0	0.3	0.6	1.2
Ga-MFI-200	4.1	2.0	0.8	1.3	1.0
Ga/deAl-Beta-100	12.7	5.6	0.8	1.5	2.5
Ga/deAl-Beta-200	19.5	9.9	2.4	4.8	1.4
Na/Ga-Beta	0.8	0.2	0.4	0.1	0.5

Table 3 The amount of deposited coke of Ga-Beta.

Catalysis	TOS [-]	W_{coke}/W_{cat} [%]
Ga-Beta-150	6	9.80
Ga-Beta-200	7	2.18

Conclusions

We synthesized high silica Ga-Beta zeolites by DGC method for catalysis of the PDH reaction. The obtained Ga-Beta zeolites showed highest propane conversion and propylene yield in Ga modified zeolites. The comparisons with other zeolite catalysts suggest that the substitution of Al into Ga, larger micropores and higher Si/Ga ratio contributed to the suppression of the cracking reaction and the excessive reactions on the PDH reaction. In addition, the increase of Si/Ga ratio resulted in the improvement of catalyst lifetime. High silica Ga-Beta can be utilized as a promising catalyst based on non-precious metals to produce propylene effectively on the PDH reaction.

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Conflicts of interest

There are no conflicts to declare.

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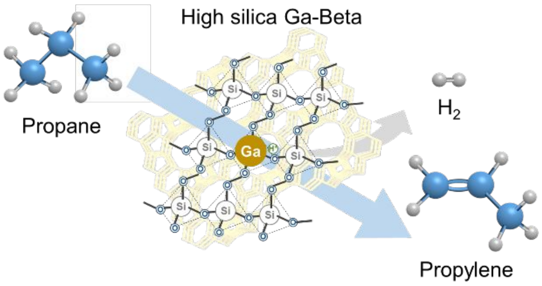

Propane is dehydrogenated over Brønsted acid sites derived from incorporated Ga in the 12-membered large micropore of *BEA-type structure