Title	Conversion of ethanol to propylene over HZSM-5(Ga) co-modified with lanthanum and phosphorous
Auther(s)	Furumoto, Yoshiyasu; Tsunoji, Nao; Ide, Yusuke; Sadakane, Masahiro; Sano, Tsuneji
Citation	Applied Catalysis A: General , 417 : 137 - 144
Issue Date	2012
DOI	10.1016/j.apcata.2011.12.034
Self DOI	
URL	http://ir.lib.hiroshima-u.ac.jp/00034804
Right	(c) 2012 Elsevier Inc. All rights reserved.
Relation	

(Revised2)

Conversion of ethanol to propylene over HZSM-5(Ga) co-modified with lanthanum and phosphorous

Yoshiyasu Furumoto, Nao Tsunoji, Yusuke Ide, Masahiro Sadakane, Tsuneji Sano*

Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan

* Corresponding author: Tel: +81-82-424-7607, Fax: +81-82-424-5494, E-mail: tsano@hiroshima-u.ac.jp

Abstract

Conversion of ethanol to propylene was carried out over HZSM-5(Ga) co-modified with lanthanum and phosphorous (La/P/HZSM-5(Ga)). The propylene yield was strongly dependent on both the La/Ga and P/Ga ratios, and the highest value of ca. 29 C-% was obtained at a P/Ga ratio of 1 and a La/Ga ratio of 0.4. FT-IR, ^{31}P MAS NMR, and ^{71}Ga MAS NMR measurements demonstrate that the introduced lanthanum reacts with the pre-introduced phosphorous to regenerate some of Brønsted acid sites (Si(OH)Ga), and accordingly, the Brønsted acid sites are homogeneously distributed within the zeolite framework. In addition, the catalytic stability as well as the catalytic activity of HZSM-5(Ga) was effectively enhanced by co-modification with lanthanum and phosphorous because of the suppression of carbonaceous deposition and elimination of gallium from the zeolite framework.

.

Keywords: Ethanol, Propylene, ZSM-5, Phosphorous, Lanthanum

1. Introduction

Owing to the increasing concerns about global warming and exhaustion of petroleum resources in recent years, the production of light olefins such as ethylene and propylene from bio-ethanol obtained by fermentation of biomass has attracted considerable attention. Light olefins are basic raw materials used in the synthesis of various chemicals and are generally produced by steam cracking of naphtha. There are many reports concerning the production of hydrocarbons such as ethylene, gasoline, and aromatics from **ethanol, aqueous ethanol and bioethanol** using solid catalysts such as zeolites [**1-13**]. However, there are few reports on the transformation of ethanol to propylene [**14-21**]. Literature reports presented thus far indicate that the distribution of products obtained in the zeolitic ethanol conversion process is strongly dependent on the acidity **(acid strength and number of acid sites)** as well as the channel structure of the zeolites. Therefore, significant effort has been devoted to controlling the acidity of zeolites by modifying them with a variety of metals including Zr, La, Sr, and P. Several structural models of the acid sites have been proposed for the zeolites modified with these metals, particularly with phosphorous [**22-25**].

We prepared isomorphously framework-substituted ZSM-5 zeolites (HZSM-5(M), M = Al, Ga, and Fe) having different acid strengths and investigated their catalytic performance in the conversion of ethanol to propylene [**26**]. High propylene yields were obtained over HZSM-5(Ga) and HZSM-5(Al), and the hydrothermal stability of HZSM-5(Ga) was found to be higher than that of HZSM-5(Al) **because of the weaker acid strength of HZSM-5(Ga).** In addition, phosphorous-modified HZSM-5(Ga) (P/HZSM-5(Ga)) showed good catalytic activity and stability because of the suppression of both carbonaceous deposition and release of gallium from the zeolite framework.

In order to further enhance the catalytic performance of P/HZSM-5(Ga), we have prepared several lanthanum- and phosphorous-co-modified HZSM-5(Ga) zeolites with various La/Ga and P/Ga ratios (La/P/HZSM-5(Ga)) and their ethanol conversion efficiency is evaluated herein. It is well known that doping of HZSM-5(Al) with lanthanum is very effective for the improvement of hydrothermal stability as well as catalytic performance [10, **15, 19**].

2. Experimental

2.1. Synthesis of isomorphously framework-substituted ZSM-5 type zeolite with gallium (HZSM-5(Ga))

Protonated ZSM-5(Ga) (HZSM-5(Ga)) having a SiO_2/Ga_2O_3 ratio of 70 was synthesized by adding gallium nitrate ($Ga(NO_3)_3 \cdot 6H_2O$, Soekawa Chemical Ind. Co. Ltd., Japan), colloidal silica (SiO_2 = 30.5 wt%, Na_2O = 0.4 wt%, H_2O = 69.1 wt%, Cataloid SI-30, JGC Catalysts and Chemicals Ltd., Japan), and tetrapropylammonium bromide (TPABr, Tokyo Chemical Ind. Co. Ltd., Japan) to a stirred solution of sodium hydroxide (Kanto Chemical Co Inc., Japan) in deionized water. The resultant hydrogel having the chemical composition of $SiO_2/Ga_2O_3 = 70$, $OH^-/SiO_2 = 0.2$, $TPABr/SiO_2 = 0.1$, and $H_2O/SiO_2 = 40$ was transferred into a 300 ml stainless-steel autoclave and stirred at 160 °C under autogenous pressure for 16 h. The precipitated crystals obtained were washed with deionized water, dried at 120 °C for one night, and calcined in air at 500 °C for 10 h to remove the organic cations occluded in the zeolite framework. The zeolite was protonated in a 0.6 M hydrochloric acid solution at 60 °C for 24 h, and calcined in air at 500 °C for 6 h. The prepared HZSM-5(Ga) had a well-defined ZSM-5 type zeolite structure, as demonstrated by the XRD pattern (Fig. 1). No diffraction peaks other than those of the ZSM-5 phase was observed. SEM observations (Fig. 1, inset) revealed a round morphology.

2.2. Preparation of lanthanum- and phosphorous-modified HZSM-5(Ga)

Phosphorous-modified HZSM-5(Ga) (P/HZSM-5(Ga)) was prepared by the impregnation method. **1 g of HZSM-5(Ga) was suspended in 5 ml of deionized water and then the desired amount of an aqueous solution of 0.02 M $(NH_4)_2HPO_4$ (Wako Pure Chemical Ind. Ltd., Japan) was added. After stirring at 60 °C for 6 h, the excess of water was removed under reduced pressure. The residue was dried at 60 °C and calcined at 500 °C for 6 h.** Lanthanum-modified HZSM-5(Ga) (La/HZSM-5(Ga)) was prepared by the same method using an aqueous solution of 0.02 M $La(NO_3)_3 \cdot 6H_2O$ (Wako Pure Chemical Ind. Ltd., Japan) instead of $(NH_4)_2HPO_4$. Lanthanum- and phosphorous-co-modified HZSM-5(Ga) (La/P/HZSM-5(Ga)) was prepared from P/HZSM-5(Ga) by impregnation with lanthanum. Characteristic peaks of lanthanum and phosphorous oxides could not be observed in the prepared zeolites. The La/Ga and P/Ga ratios and BET surface areas of the prepared zeolites are listed in Table

1.

2.3. Characterization

X-ray diffraction (XRD) patterns of the solid products were obtained using a powder X-ray diffractometer (Bruker D8 Advance) with graphite monochromatized Cu Kα radiation at 40 kV and 30 mA. The SiO_2/Ga_2O_3 ratio was determined via X-ray fluorescence (XRF, Philips PW 2400). A fixed amount of the sample (0.5 g) was fused with 5 g of dilithium tetraborate ($Li_2B_4O_7$) at 1100 °C. The crystal morphology was observed using scanning electron microscopy (SEM, Hitachi S-4800). Thermal analyses were carried out using a TG/DTA apparatus (SSC/5200 Seiko Instruments). The sample (ca. 3 mg) was heated from room temperature to 800 °C at a rate of 10 °C/min in an air flow (50 ml/min). ^{31}P MAS NMR and ^{71}Ga MAS NMR spectra were recorded at 600 MHz on a Varian 600 spectrometer using a 3.2 mm diameter zirconia rotor with spinning at 15 kHz. The spectra were obtained with 2.8 μs pulses, 15 s recycle delay, and 10,000 scans for ^{31}P MAS NMR, and 2.8 μs pulses, 0.1 s recycle delay, and 400,000 scans for ^{71}Ga MAS NMR. $NH_4H_2PO_4$ and $Ga(NO_3)_3 \cdot 6H_2O$ were used as chemical shift references. Nitrogen adsorption isotherms were obtained at -196 °C using a conventional volumetric apparatus (BELSORP-max, Bel Japan). Prior to performing the adsorption measurements, the calcined samples (ca. 0.1 g) were evacuated at 400 °C for 10 h. IR spectra were recorded at room temperature on an FT-IR spectrometer (JEOL JIR-7000) with a resolution of 4 cm^{-1}. Measurements in the OH group stretching region were carried out by pressing the sample into a self-supporting thin wafer (ca. 6.4 mg/cm^2), which was placed in a quartz IR cell with CaF_2 windows. Prior to carrying out the measurements, each sample was dehydrated under vacuum at 400 °C for 2 h.

2.4 Ethanol conversion

Zeolitic ethanol conversion was carried out at a reaction temperature of 500 °C with a contact time (W/F) value of 0.02 g_{cat}/ml/min in an atmospheric-pressure flow system. The required amount of zeolite (12–24 mesh) was retained by placing quartz wool at the center of a quartz reactor with a 10 mm inner diameter. A thermocouple inserted at the center of the catalyst bed was used to measure the temperature during the reaction. The catalyst was activated at 500 °C for 1 h under nitrogen flow prior to carrying out the reaction. Ethanol (>99.5%, Wako Pure Chemical Ind. Ltd., Japan) was pumped into the vaporizer and mixed with N_2 at a total flow rate of 20 ml/min (C_2H_5OH/N_2 = 50/50 mol%). The gaseous products were analyzed using on-time GC equipped with TCD- and FID-type detectors on a Shincarbon ST (Shinwa Chem. Ind. Ltd., Japan) column for

N_2, H_2, and CO_2; on a Gaskropack54 (GL Sciences, Japan) column for ethanol; and on a RT-alumina PLOT (Restek, USA) column for C_1–C_4 hydrocarbons. The product yields were calculated using N_2 as an internal standard.

3. Results and Discussion

3.1. Effect of La/Ga ratio on ethanol conversion over La/P/HZSM-5(Ga) with P/Ga ratio of 0.2

Our previous study on ethanol conversion over P/HZSM-5(Ga) indicated that the oligomerization of ethylene produced by the dehydration of ethanol was suppressed by phosphorous modification of the zeolite, given that the propylene yield increased with an increase in the P/Ga ratio and reached a maximum value at a P/Ga ratio of 0.2–0.3, whereas the ethylene yield increased monotonously with the P/Ga ratio [**26**]. On the basis of this background, we first examined the effect of lanthanum modification on P/HZSM-5(Ga) having a P/Ga ratio of 0.2. Figure 2 shows the relationship between the La/Ga ratio and the product yields when the ethanol conversion was carried out at 500 ˚C and W/F of 0.02 g_{cat}/ml/min. Regardless of the La/Ga ratio, 100% ethanol conversion was achieved with all of the catalysts evaluated. The propylene and butene yields decreased monotonously with increasing La/Ga ratio, whereas the yields of the

C_2–C_4 paraffins and the C_5^+ fraction including aromatics increased with increasing La/Ga ratio. The ethylene yield decreased as the La/Ga ratio increased and reached a minimum value at a La/Ga ratio of 0.05–0.1, indicating that the oligomerization of ethylene produced by the dehydration of ethanol was enhanced by doping of the P/HZSM-5(Ga) zeolite with small amounts of lanthanum. Literature indicates that phosphorous modification of HZSM-5(Al) decreases the number of strong Brønsted acid sites [8, **21**]. In comaprison, the current observations suggest that the enhanced oligomerization acitivity of the lanthanum modified P/HZSM-5(Ga) is due to regeneration of strong acid sites.

To verify this postulate, FT-IR spectral evaluation of La/P/HZSM-5(Ga) was performed within the OH region. The spectra of P/HZSM-5(Ga)(P/Ga ratio = 0.2) and La/P/HZSM-5(Ga)(P/Ga ratio = 0.2; La/Ga ratios = 0.1, 0.15) presented in Figure 3 show two sharp peaks at approximately 3740 and 3620 cm^{-1}. The former peak was assigned to the isolated silanol group, and the later peak was attributed to an acidic bridging OH group of Si(OH)Ga, i.e., a Brønsted acid site [**27**]. There was no difference in the intensity of the peak at 3620 cm^{-1} for P/HZSM-5(Ga) and La/P/HZSM-5(Ga), which suggests that the peak intensity of the Brønsted acid site is hardly influenced by small amounts of phosphorous and lanthanum. Therefore, the effect of lanthanum modification was investigated at a higher P/Ga ratio in the following experiments using P/HZSM-5(Ga) with P/Ga ratio of 1.

3.2. Effect of La/Ga ratio on ethanol conversion over La/P/HZSM-5(Ga) with P/Ga ratio of 1

Figure 4 shows the relationship between the La/Ga ratio of La/P/HZSM-5(Ga) and the product yields. As observed for the P/Ga ratio of 0.2 (previous section), the ethanol conversion was 100% for all zeolites. At the P/Ga ratio of 1, the La/Ga ratio dependence of the product yields was slightly different from that of P/HZSM-5(Ga) with a P/Ga ratio of 0.2. In contrast with the propylene yield at a P/Ga ratio of 0.2, the propylene yield increased with increasing La/Ga ratio and reached a maximum value of ca. 29 C-% at the La/Ga ratio of ca. 0.4, whereas the ethylene yield decreased remarkably. The yields of the C_2–C_4 paraffins and the C_5^+ fraction increased monotonously with increasing La/Ga ratio. These results suggest that lanthanum modification enhances the oligomerization of ethylene and the formation of aromatics through hydrogen transfer reaction of higher olefins. Figure 5 shows the OH region of the FT-IR spectra of La/P/HZSM-5(Ga) with various La/Ga ratios. It is clear that the intensity of the peak at 3620 cm^{-1} assigned to the Brønsted acid sites increased with inceasing La/Ga ratio, suggesting regeneration of Brønsted acid sites as a result of lanthanum modification. A similar phenomenon was observed for P/HZSM-5(Al) modified by lanthanum doping [**28**]. The small peak at ca. 3670 cm^{-1} in the spectrum of P/HZSM-5(Ga) without lanthanum doping is probably attributed to OH groups of phosphorous species bonded to the zeolitic hydroxyls [**29, 30**].

The ^{31}P MAS NMR spectra were acquired in order to gain insight into the nature of the phosphorous species in the zeolites. Figure 6 shows the ^{31}P MAS NMR spectra of P/HZSM-5(Ga) and La/P/HZSM-5(Ga) with a La/Ga ratio of 0.4. Broad peaks in the range from 0 to -50 ppm were observed for P/HZSM-5(Ga), which are related to monomeric and **condensed** phosphorous species [**28, 31, 32**]. On the other hand, La/P/HZSM-5(Ga) shows an intense peak at ca. -3.4 ppm which is **assigned** to $LaPO_4$, generated by interaction of introduced lantanum with the phosphorous bonded to the zeolitic hydroxyls, resulting in regeneration of Brønsted acid sites (Si(OH)Ga) [**28**]. Because weak peaks related to monomeric and condensed phosphorous species were also observed in the range from 0 to -50 ppm, it can be deduced that a portion of the phosphorous still interacted with the zeolite framework.

^{71}Ga MAS NMR measurements were subsequently performed to evaluate the chemical states of the gallium species in the zeolites. Figure 7 shows the ^{71}Ga MAS

NMR spectra of P/HZSM-5(Ga) and La/P/HZSM-5(Ga). An intense peak at ca. 160 ppm, assigned to tetrahedral framework gallium species, was observed in the spectrum of P/HZSM-5(Ga). A weak peak was also observed at ca. -50 ppm, which can be assigned to the tetrahedral gallium **distorted** by phosphorous [**28, 30**]. After doping P/HZSM-5(Ga) with lanthanum, a clear increase in the peak intensity at ca. 160 ppm was observed. Simultaneously, the peak at ca. -50 ppm disappeared. Xue et al. reported that mixing of phosphorous-modified HZSM-5(Al) with alumina as binder resulted in leaching of phosphorous from the phosphorous-modified zeolite to the alumina binder [**30**]. The present results also indicate that the introduced lanthanum interacted with the pre-introduced phosphorous to release the tetrahedral gallium species, i.e., regeneration of Brønsted acid sites.

It is generally accepted that the product distribution in the zeolitic ethanol conversion process is strongly dependent on the acidity as well as the channel structure of the zeolite and that ethanol is considered to be first converted to ethylene and subsequently to higher hydrocarbons. The initial ethylene and propylene yields are thought to be related to the oligomerization capacity of the zeolites on the acid sites. Therefore, the effect of ethylene consumption on the propylene yield was investigated. The propylene yield was plotted against **the ethylene consumption rate (%, 100 - yield of ethylene)**, as shown in Figure 8. To obtain a variety of ethylene consumption values, the ethanol conversion reaction was carried out at 500 °C by varying the W/F ratio. For all zeolite catalysts of HZSM-5(Ga), P/HZSM-5(Ga) with a P/Ga ratio of 0.2, and La/P/HZSM-5(Ga) with a La/Ga ratio of 0.4 and a P/Ga ratio of 1, the propylene yield increased with an increase in the ethylene consumption rate and reached a maximum yield at an ethylene consumption rate of ca.70%. This strongly indicates that there is no difference in the acidic strength of the acid sites of the three catalysts. **Although a slight difference was observed in the aromatic yields of P/HZSM-5(Ga)(15.8 C-%) and La/P/HZSM-5(Ga)(14.2 C-%) after 30 min of time-on-stream, this difference might be explained by the difference in local distribution of protonic sites. Sazama et al. previously reported that the aluminum distribution in the framework of HZSM-5(Al) affects the product composition during 1-butene cracking [33]. Close proximity of the aluminum atoms enhances the hydrogen transfer reaction leading to aromatics. Therefore, it seems that Brønsted acid sites (Si(OH)Ga) are homogeneously distributed within the zeolite framework of La/P/HZSM-5(Ga).**

In order to get information concerning an effect of $LaPO_4$ generated within the zeolite on ethanol conversion, HZSM-5(Ga) was physically mixed with $LaPO_4$, $LaPO_4$/Ga ratio of 0.4, and the ethanol conversion efficiency was investigated.

$LaPO_4$ was prepared according to the literature [34]. The distribution of products was C_2H_4 of 32 .2 C-%, C_3H_6 of 23.4 C-%, C_4H_4 of 14.7 C-%, and C_5^+ of 20.4 C-%. There was no difference in the product distribution between the $LaPO_4$/HZSM-5(Ga) and the HZSM-5(Ga) in Table 2, indicating that $LaPO_4$ generated does not affect the acidity of HZSM-5(Ga).

On the basis of the results obtained above, the surface structure of HZSM-5(Ga) co-modified with lanthanum and phosphorous could be proposed as follows. Figure 9 shows a schematic illustration of the processes accompanying introduction of lanthanum into P/HZSM-5(Ga).

(1) In the case of a P/Ga ratio < 1 (Figure 9(A))

At least two types of acidic sites are present in the P/HZSM-5(Ga). The first type is the surface P-OH groups generated by introduction of phosphorous. The other type is native OH groups of the Brønsted acid sites (Si(OH)Ga) in the zeolite, which are not modified by phosphate. Upon introduction of lanthanum ions into the P/HZSM-5(Ga) zeolite, the lanthanum ions interact with the surface P-OH groups to release some bridging OH groups through formation of $LaPO_4$. Further introduction of lanthanum results in exchange of zeolitic protons with the lanthanum ions to generate La-OH groups, which might be new acidic sites. The product distribution for ethanol conversion over La/HZSM-5(Ga) with a La/Ga ratio of 0.4 after 30 min of time-on-stream was compared with those of HZSM-5(Ga) and P/HZSM-5(Ga). The data presented in Table 2 show that similar to phosphorous modification, lanthanum modification also affected the product distribution; the high ethylene yield indicates the reduction of surface acidity in a similar way to the phosphorous modification.

(2) In the case of a P/Ga ratio > 1 (Figure 9(B))

In this instance, the native surface OH groups on the surface of P/HZSM-5(Ga) are fully completely replaced with P-OH groups. The introduced lanthanum ions only interact with the surface P-OH groups to release zeolitic protons when the number of lanthanum ions is less than that of the pre-introdued phosphorous. Accordingly, the Brønsted acid sites (Si(OH)Ga) are homogeneously distributed within the zeolite framework.

3.3 Catalyst stability

In general, the deactivation of zeolite catalysts occurs predominantly by two main mechanisms: one is the poisoning of acid sites and/or the pore blocking due to the accumulation of carbonaceous deposits and the other is the structural degradation of the zeolite due to the elimination of the zeolite framework metals. Therefore, the catalytic stability of La/PHZSM-5(Ga) was investigated. Figure 10 shows the time-on-stream of propylene yield over HZSM-5(Ga), P/HZSM-5(Ga) with a P/Ga ratio of 0.2, and La/P/HZSM-5(Ga) with a P/Ga ratio of 1 and a La/Ga ratio of 0.4. The reaction conditions were fixed at 500 °C and W/F of 0.02 g_{cat}/ml/min. During the catalyst durability tests, these zeolite catalysts were regenerated two times by calcination at 500 °C for 10 h in air. For these catalysts, the ethanol conversion was 100 % even after 24 h of time-on-stream. The propylene yield for the unmodified HZSM-5(Ga) decreased rapidly with the time-on-stream and did not exhibit the initial value even after regeneration. On the other hand, the propylene yield hardly changed for the modified HZSM-5(Ga). **As can be seen in Figure 11,** with the exception of propylene, the product yields changed slightly with time-on-stream in the first run of La/P/HZSM-5(Ga), especially for ethylene. **We do not have enough data to explain the behavior at the present time.** The amounts of carbonaceous deposits after 8 h of time-on-stream as evaluated by TG analysis were as follows: 3.0 wt% for HZSM-5(Ga), 1.8 wt% for P/HZSM-5(Ga), and 0.8 wt% for La/P/HZSM-5(Ga).

Figure 12 shows the ^{71}Ga MAS NMR spectra of HZSM-5(Ga) and La/P/HZSM-5(Ga) before and after ethanol conversion. In the case of HZSM-5(Ga) (Fig. 12(A)), the intensity of the peak at ca. 160 ppm assigned to tetrahedral framework gallium species was considerably reduced after the reaction relative to before the reaction. The decrease in the peak intensity indicates that elimination of framework gallium by water generated by dehydration of ethanol and/or burning of carbonaceous deposits occurred during the reaction and/or regeneration process of zeolite catalysts.

However, no increase was observed in the intensity of the peak at around 0 ppm assigned to the extra-framework gallium species. Because the extra-framework gallium species appear to be non-uniform and exist in different states, the peak corresponding to the extra-framework gallium species is broadened to the extent that the peak can no longer be observed in a normal single-pulse experiment, and is undetectable by NMR. The presence of NMR-invisible aluminum species is often observed for highly siliceous zeolites such as ZSM-5(Al) **[35, 36].** In the case of La/P/HZSM-5(Ga) (Fig. 7(B)), on the other hand, there was only a slight decrease in the intensity of the peak at ca. 160 ppm, indicating that the hydrothermal stability of the zeolite was improved by co-modification with lanthanum and phosphorous relative to unmodified HZSM-5(Ga).

^{31}P MAS NMR measurements were also carried out for P/HZSM-5(Ga) and La/P/HZSM-5(Ga) before and after the reaction in order to clarify the effects of La doping on hydrothermal stability of the zeolite with pre-introduced phosphorous. The hydrothermal stability of phosphorous in P/HZSM-5(Ga) and La/P/HZSM-5(Ga) was vastly different. Condensed phosphorus species were clearly observed from -20 to -50 ppm for P/HZSM-5(Ga) after the reaction, whereas there was only a slight increase in the intensity of the condensed phosphorous species for La/P/HZSM-5(Ga); that is, the introduced lanthanum prohibits the loss of phosphorus from the zeolite surface.

On the basis of the results presented, it was found that co-modification of HZSM-5(Ga) with lanthanum and phosphorous is very effective for improvement of the catalytic activity and stability of the zeolite.

4. Conclusions

The catalytic performance of La/P/HZSM-5(Ga) having various P/Ga and La/Ga ratios in ethanol conversion was investigated. In the case of a P/Ga ratio < 1, the propylene yield decreased with increasing La/Ga ratio. On the other hand, in the case of a P/Ga ratio > 1, the propylene yield increased with the La/Ga ratio and reached a maximum value of ca. 29 C-% at the La/Ga ratio of 0.4. FT-IR, ^{31}P MAS NMR, and ^{71}Ga MAS NMR measurements revealed that introduced lanthanum reacts with the pre-introduced phosphorous with consequent regeneration of some of the Brønsted acid sites. Accordingly, Brønsted acid sites (Si(OH)Ga) are homogeneously distributed within the zeolite framework, which is effective for the formation of light olefins rather than aromatics and paraffins. Catalytic durability tests demonstrated that co-modified La/P/HZSM-5(Ga) exhibited enhanced catalytic stability relative to native HZSM-5(Ga) and singly modified P/HZSM-5(Ga) because of the suppression of carbonaceous deposition and elimination of gallium from the zeolite framework.

Acknowledgment

This work was supported by a New Energy and Industrial Technology Development Organization (NEDO) grant.

References

[1] V.R. Choudhary, V.S. Nayak, Zeolites 5 (1985) 325-328.

[2] S.K. Saha, S. Sivasanker, Catal. Lett. 15 (1992) 413-418.

[3] E. Costa, A. Uguina, J. Aguado, P.J. Hernandez, Ind. Eng. Chem. Process. Des. Dev. 24 (1985) 239-244.

[4] A.K. Talukdar, K.G. Bhattacharyya, S. Sivasanker, Appl. Catal. A: Gen. 148 (1997) 357-371.

[5] **A.T. Aguayo**, A.G. Gayubo, A.M. Tarrio, A. Atutxa, J. Bilbao, J. Chem. Technol. Biotechnol. 77 (2002) 211-216.

[6] M. Inaba, K. Murata, M. Saito, **I. Takahara**, React. Kinet. Catal. Lett. 88 (2006) 135-142; **Green Chem. 9 (2007) 638-646.**

[7] V. Calsavara, M.L. Baesso, N.R.C. Fernandez-Machado, Fuel 87 (2008) 1628-1636.

[8] D. Zhang, R. Wang, X. Yang, Catal. Lett. 124 (2008) 384-391.

[9] F. Ferreria-Madeira, N.S. Gnep, P. Magnoux, S. Maury, N. Gadran, Appl. Catal. A: Gen. 367 (2009) 39-46.

[10] J. Ouyang, F. Kong, G. Su, Y. Hu, Q. Song, Catal. Lett. 132 (2009) 64-74.

[11] S. Sugiyama、Y. Kato, T. Wada、S. Ogawa, K. Nakagawa, K.-I. Sotowa, Top. Catal. 53 (2010) 550-554.

[12] A.G. Gayubo, A. Ainhoa, B. Valle, A.T. Aguayo, M. Olazar, J. Bilbao, Fuel 89 (2010) 3365-3372.

[13] M. Inaba, K. Murata, I. Takahara, K. Inoue, J. Chem. Technol. Biotechnol. 86 (2011) 95-104.

[**14**] H. Oikawa, Y. Shibata, K. Inazu, Y. Iwase, K. Murai, S. Hyodo, G. Kobayashi, T. Baba, Appl. Catal. A: Gen. 312 (2006) 181-185.

[**15**] K. Murata, M. Inaba, T. Takahara, J. Jpn. Petrol. Inst. 51 (2008) 234-239.

[**16**] Q. Zhu, J.N. Kondo, S. Inagakli, T. Tatsumi, Top. Catal. 52 (2009) 1272-1280.

[**17**] T. Yamazaki, N. Kikuchi, M. Katoh, Y. Okada, T. Yoshikawa, M. Wada, J. Jpn. Petrol. Inst. 52 (2009) **239-247**.

[**18**] Z. Song, A. Takahashi, N. Mimura, T. Fujitani, Catal. Lett. 131 (2009) 364-369.

[**19**] K. Inoue, K. Okabe, M. Inaba, I. Takahara, K. Murata, Reac. Kinet. Mech. Cat. 101 (2010) 477-489.

[**20**] D. Goto, Y. Harada, Y. Furumoto, A. Takahashi, T. Fujitani, Y. Oumi, M. Sadakane, T. Sano, Appl. Catal. A: Gen. 383 (2010) 89-95.

[**21**] Z. Song, A. Takahashi, I. Nakamura, T. Fujitani, Appl. Catal. A: Gen. 384 (2010) 201-205.

[**22**] T. Blasco, A. Corma, J. Martinez-Triguero, J. Catal. 237 (2006) 267-277.

[**23**] W.W. Kaeding, S.A. Butter, J. Catal. 61 (1980) 155-164.

[**24**] J.C. Vedrine, A. Auroux, P. Dejaifve, V. Ducarme, H. Hoser, S. Zhou, J. Catal. 73 (1982) 147-160.

[**25**] J.A. Lercher, G. Rumolmayr, Appl. Catal. 25 (1986) 215-222.

[**26**] Y. Furumoto, Y. Harada, N. Tsunoji, A. Takahashi, T. Fujitani, Y. Ide, M. Sadakane, T. Sano, Appl. Catal. A: Gen. 399 (2011) 262-267.

[**27**] C.T-W. Chu, C.D. Chung, J. Phys. Chem. 89 (1985) 1569–1571.

[**28**] N. Xue, N. Liu, L. Nie, Y. Yu, M. Gu, L. Peng, X. Guo, W. Ding, J. Mol. Catal. A:

Chem. 327 (2010) 12-19.

[**29**] A. Jentys, G. Rumplmayr, J.A. Lercher, Appl. Catal. 53 (1989) 299-312.

[**30**] N. Xue, R. Olindo, J. A. Lercher, J. Phys. Chem. C 114 (2010) 15763-15770.

[**31**] N. Xue, X. Chen, L. Nie, X. Guo, W. Ding, Y. Chen, M. Gu, Z. Xie, J. Catal. 248 (2007) 20-28.

[**32**] M. Göhlich, W. Reschetilowski, S. Paasch, Micropor. Mesopor. Mater. 142 (2011) 178-183.

[**33**] P. Sazama, J. Dědeček, V. Gábová, B. Wichterlová, G. Spoto, S. Bordiga, J. Catal. 254 (2008) 180-189.

[34] H. Onoda, Y. Ishima, A. Takenaka, I. Tanaka, Mater. Res. Bull. 44 (2009) 1712 -1716.

[35] E. Loeffler, U. Lohse, Ch. Peuker, G. Oehlmann, L.M. Kustov, V.L. Zholobenko, V.B. Kazansky, Zeolites 10 (1990) 266-271.

[36] S.M. Alexander, D.M. Bibby, R.F. Howe, R.H. Meinhold, Zeolites 13 (1993) 441-447.

Table 1 Characteristics of lanthanum- and phosphorous-co-modified HZSM-5(Ga) with SiO_2/Ga_2O_3 ratio of 70.

Sample no.	Catalyst	P/Ga[a]	La/Ga[a]	BET surface area[b] /m^2g^{-1}
1	HZSM-5(Ga)	-	-	389
2	P/HZSM-5(Ga)	0.2	-	351
3	La/P/HZSM-5(Ga)	0.2	0.05	377
4	La/P/HZSM-5(Ga)	0.2	0.1	357
5	La/P/HZSM-5(Ga)	0.2	0.15	357
6	P/HZSM-5(Ga)	1.0	-	340
7	La/P/HZSM-5(Ga)	1.0	0.2	331
8	La/P/HZSM-5(Ga)	1.0	0.3	336
9	La/P/HZSM-5(Ga)	1.0	0.4	355
10	La/P/HZSM-5(Ga)	1.0	0.5	327
11	La/P/HZSM-5(Ga)	1.0	0.7	338
12	La/HZSM-5(Ga)	-	0.4	346

[a] Determined by XRF.

[b] Determined by the BET method.

Table 2 Product distributions of ethanol conversion over HZSM-5(Ga), P/HZSM-5, and La/HZSM-5(Ga).

Sample no.	Catalyst	C_2H_4	C_3H_6	C_4H_8	C_2-C_4 paraffins	C_5^+
1	HZSM-5(Ga)	28.1	24.7	14.4	11.2	21.6
2	P/HZSM-5(Ga)	31.9	27.1	17.6	7.6	15.8
6	P/HZSM-5(Ga)	92.3	4.7	3.0	0	0
12	La/HZSM-5(Ga)	71.6	13.3	5.8	3.0	6.3

Temp. = 500 ˚C , W/F = 0.02 g_{cat}/ml/min

Figure Captions

Figure 1 XRD pattern and SEM image of as-synthesized HZSM-5(Ga).

Figure 2 Effect of La/Ga ratio on product yields of ethanol conversion over La/P/HZSM-5(Ga) with P/Ga ratio of 0.2.

Temp. = 500 ˚C, W/F = 0.02 g_{cat}/ml/min

Figure 3 FT-IR spectra of (a) P/HZSM-5(Ga) with P/Ga ratio of 0.2 and La/P/HZSM-5(Ga) with P/Ga ratio of 0.2 and La/Ga ratios of (b) 0.1 and (c) 0.15.

Figure 4 Effect of La/Ga ratio on product yields of ethanol conversion over La/P/HZSM-5(Ga) with P/Ga ratio of 1.0.

Temp. = 500 ˚C, W/F = 0.02 g_{cat}/ml/min

Figure 5 FT-IR spectra of (a) P/HZSM-5(Ga) with P/Ga ratio of 1 and La/P/HZSM-5(Ga) with P/Ga ratio of 1 and La/Ga ratios of (b) 0.4 and (c) 0.7.

Figure 6 ^{31}P MAS NMR spectra of (a) P/HZSM-5(Ga) with P/Ga ratio of 1.0 and (b) La/P/HZSM-5(Ga) with P/Ga ratio of 1.0 and La/Ga ratio of 0.4.

Figure 7 ^{71}Ga MAS NMR spectra of (a) P/HZSM-5(Ga) with P/Ga ratio of 1.0 and (b) La/P/HZSM-5(Ga) with P/Ga ratio of 1.0 and La/Ga ratio of 0.4.

Figure 8 Relationship between consumption rate of C_2H_4 and yield of C_3H_6 over (○) HZSM-5(Ga), (▲) P/HZSM-5(Ga), and (◇) La/P/HZSM-5(Ga).

Figure 9 Change in the structure of modified acid sites during introduction of La into P/HZSM-5(Ga) with P/Ga ratios of (A) 0.2 and (B) 1.0.

P: Phosphorous species interacting with Brønsted acid sites.

Figure 10 Time-on-stream of C_3H_6 yield for ethanol conversion over (△) HZSM-5(Ga), (◆) P/HZSM-5(Ga) with P/Ga ratio of 0.2, and (○) La/P/HZSM-5(Ga) with P/Ga ratio of 1.0 and La/Ga ratio of 0.4.

Catalysts were regenerated by calcination at 500 ˚C for 10 h in air.

Temp. = 500 ˚C, W/F = 0.02 g_{cat}/ml/min

Figure 11 Time-on-stream of product yields for ethanol conversion over La/P/HZSM-5(Ga) with P/Ga ratio of 1.0 and La/Ga ratio of 0.4.

Catalysts were regenerated by calcination at 500 ˚C for 10 h in air.

Temp. = 500 ˚C, W/F = 0.02 g_{cat}/ml/min

Figure 12 ^{71}Ga MAS NMR spectra of (A) HZSM-5(Ga) and (B) La/P/HZSM-5(Ga) with P/Ga ratio of 1.0 and La/Ga ratio of 0.4 (a) before and (b) after 24 h of time-on-stream.

Figure 13 ^{31}P MAS NMR spectra of (A) P/HZSM-5(Ga) with P/Ga ratio of 0.2 and (B) La/P/HZSM-5(Ga) with P/Ga ratio of 1.0 and La/Ga ratio of 0.4 (a) before and (b) after of 24 h of time-on-stream.

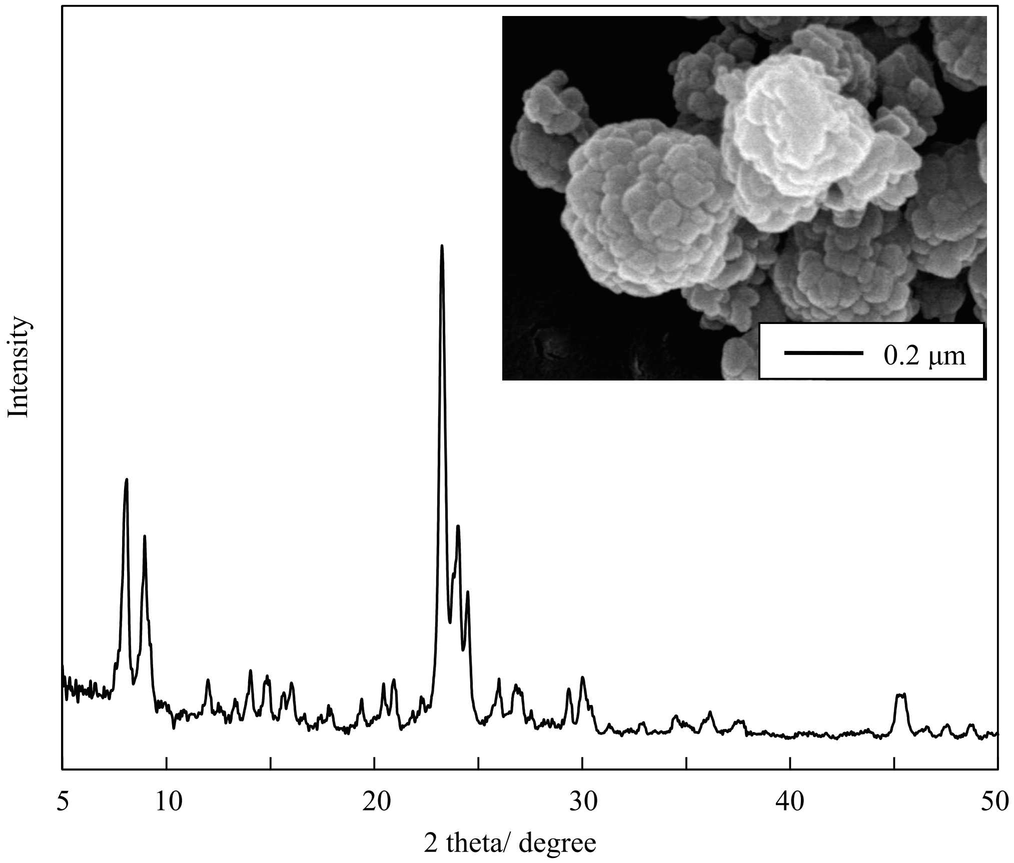

Figure 1 XRD pattern and SEM image of as-synthesized HZSM-5(Ga).

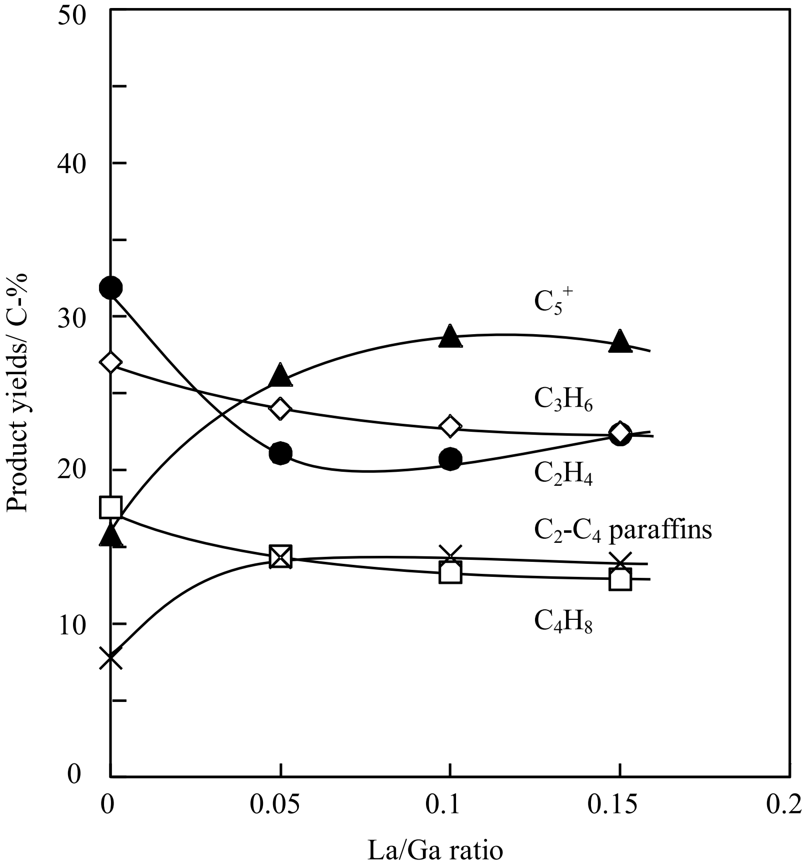

Figure 2 Effect of La/Ga ratio on product yields of ethanol conversion over La/P/HZSM-5(Ga) with P/Ga ratio of 0.2.

Temp. = 500 ˚C, W/F = 0.02 g_{cat}/ml/min

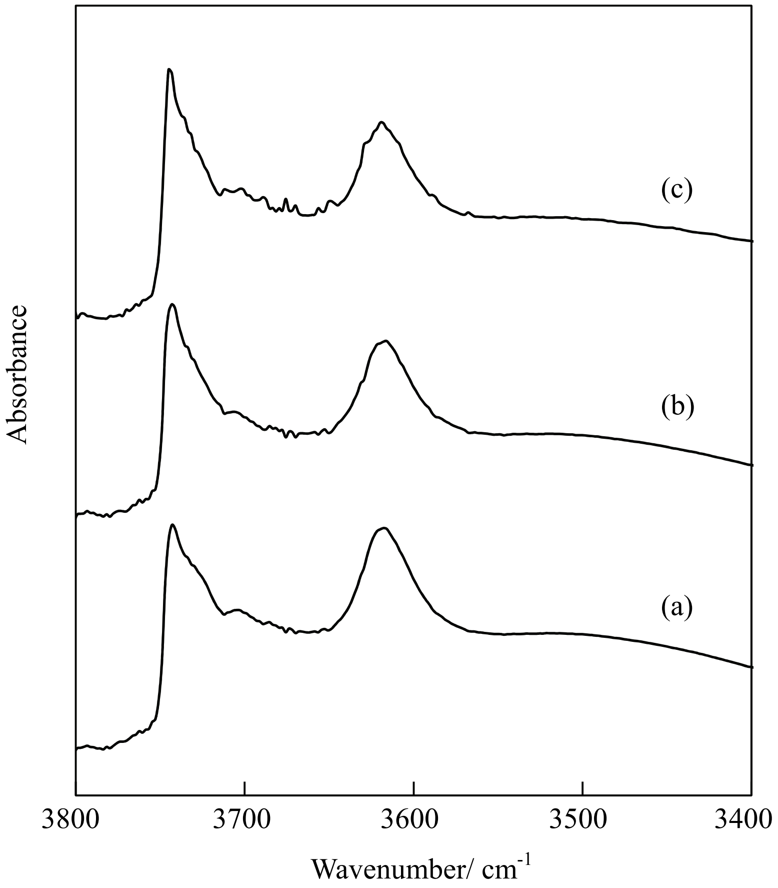

Figure 3 FT-IR spectra of (a) P/HZSM-5(Ga) with P/Ga ratio of 0.2 and La/P/HZSM-5(Ga) with P/Ga ratio of 0.2 and La/Ga ratios of (b) 0.1 and (c) 0.15.

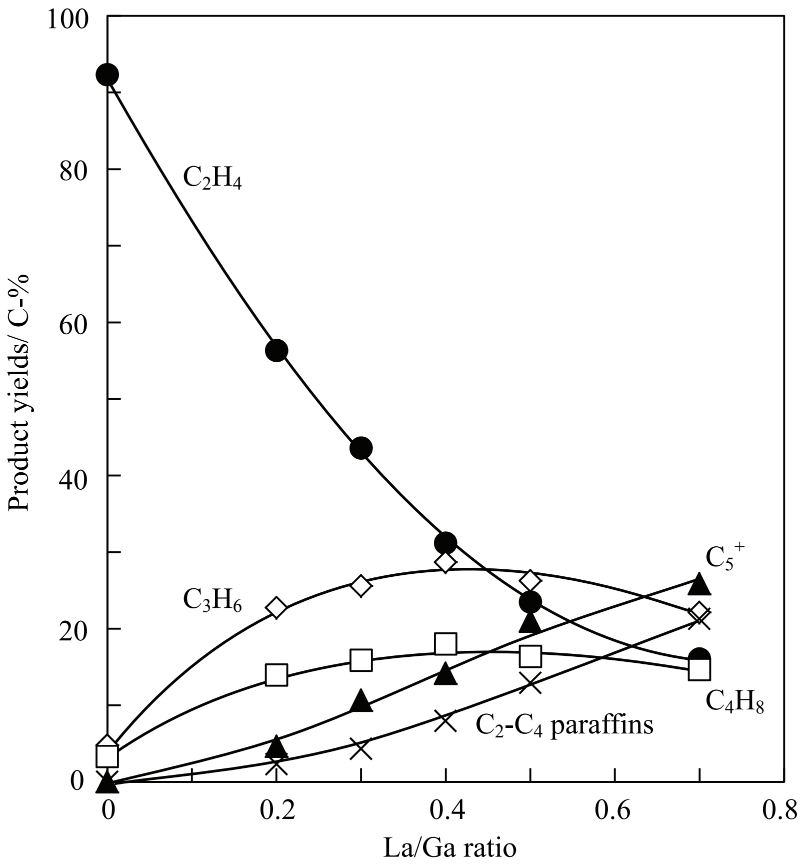

Figure 4 Effect of La/Ga ratio on product yields of ethanol conversion over La/P/HZSM-5(Ga) with P/Ga ratio of 1.0.

Temp. = 500 ˚C, W/F = 0.02 g_{cat}/ml/min

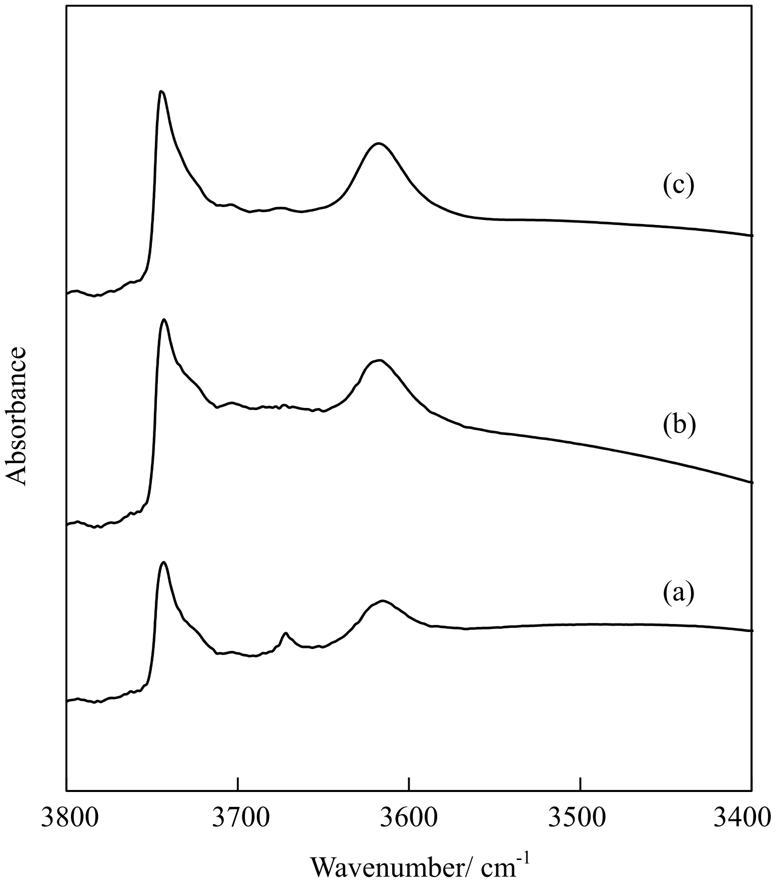

Figure 5 FT-IR spectra of (a) P/HZSM-5(Ga) with P/Ga ratio of 1 and La/P/HZSM-5(Ga) with P/Ga ratio of 1 and La/Ga ratios of (b) 0.4 and (c) 0.7.

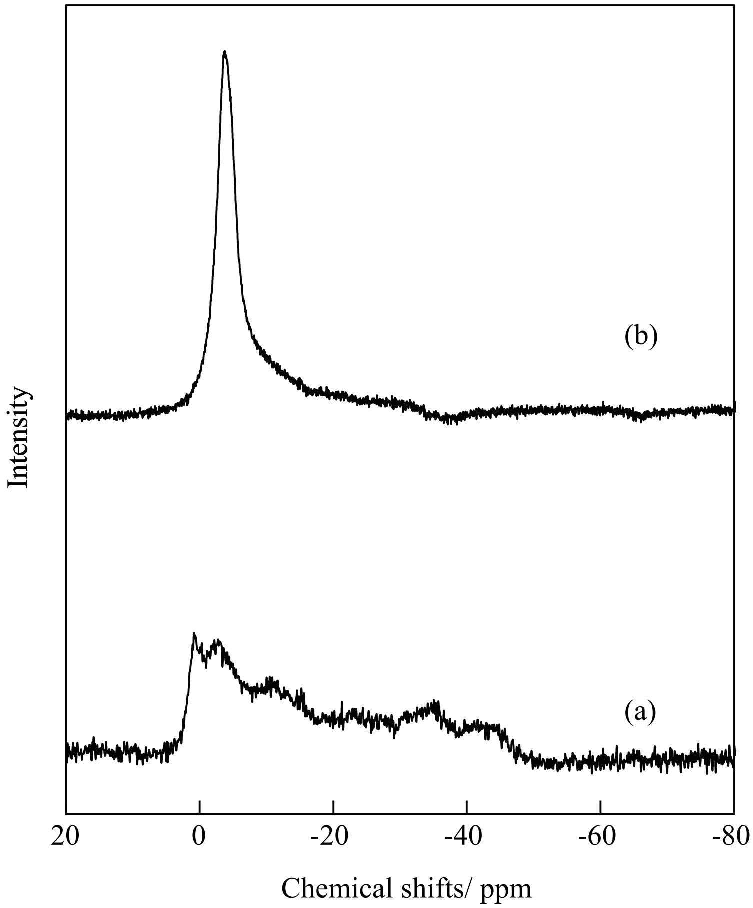

Figure 6 ^{31}P MAS NMR spectra of (a) P/HZSM-5(Ga) with P/Ga ratio of 1.0 and (b) La/P/HZSM-5(Ga) with P/Ga ratio of 1.0 and La/Ga ratio of 0.4.

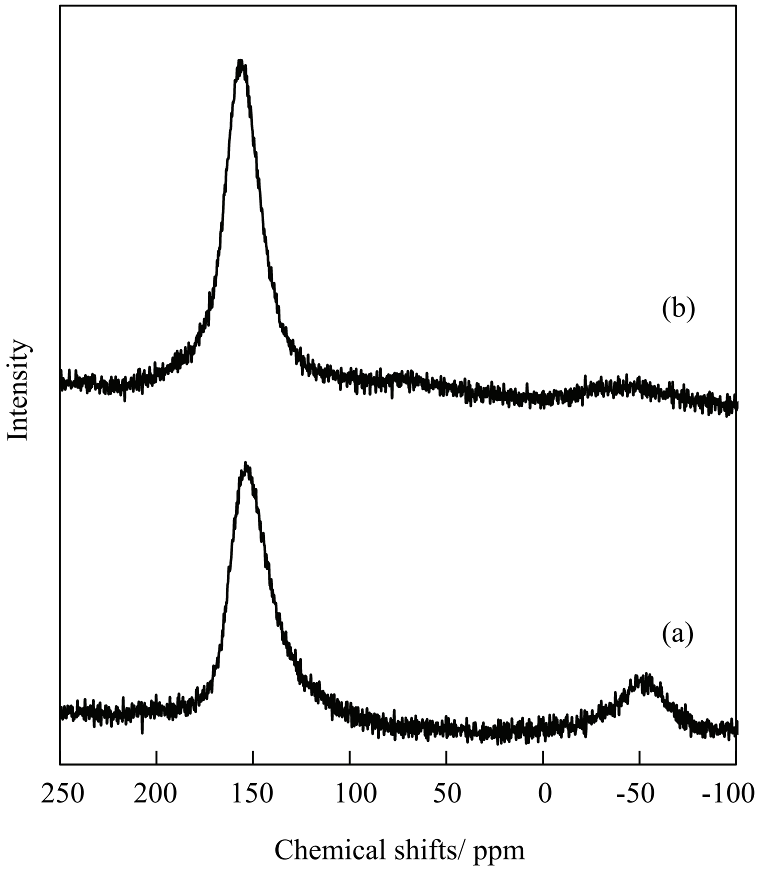

Figure 7 ^{71}Ga MAS NMR spectra of (a) P/HZSM-5(Ga) with P/Ga ratio of 1.0 and (b) La/P/HZSM-5(Ga) with P/Ga ratio of 1.0 and La/Ga ratio of 0.4.

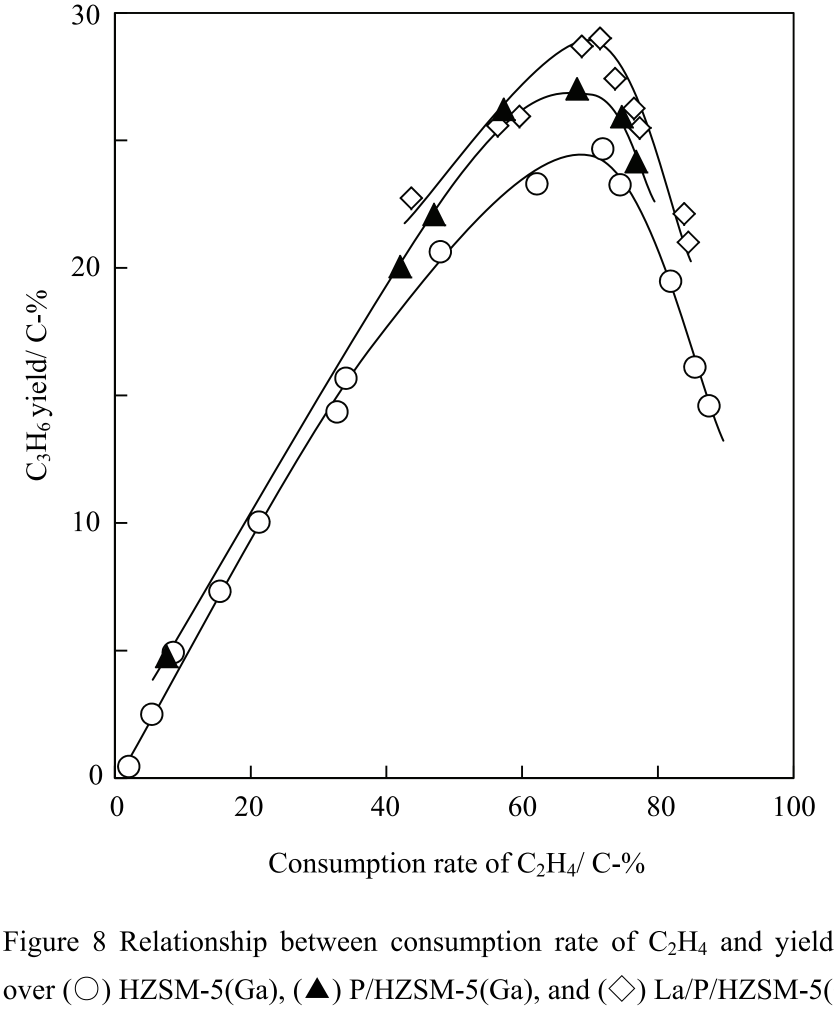

Figure 8 Relationship between consumption rate of C_2H_4 and yield of C_3H_6 over (○) HZSM-5(Ga), (▲) P/HZSM-5(Ga), and (◇) La/P/HZSM-5(Ga).

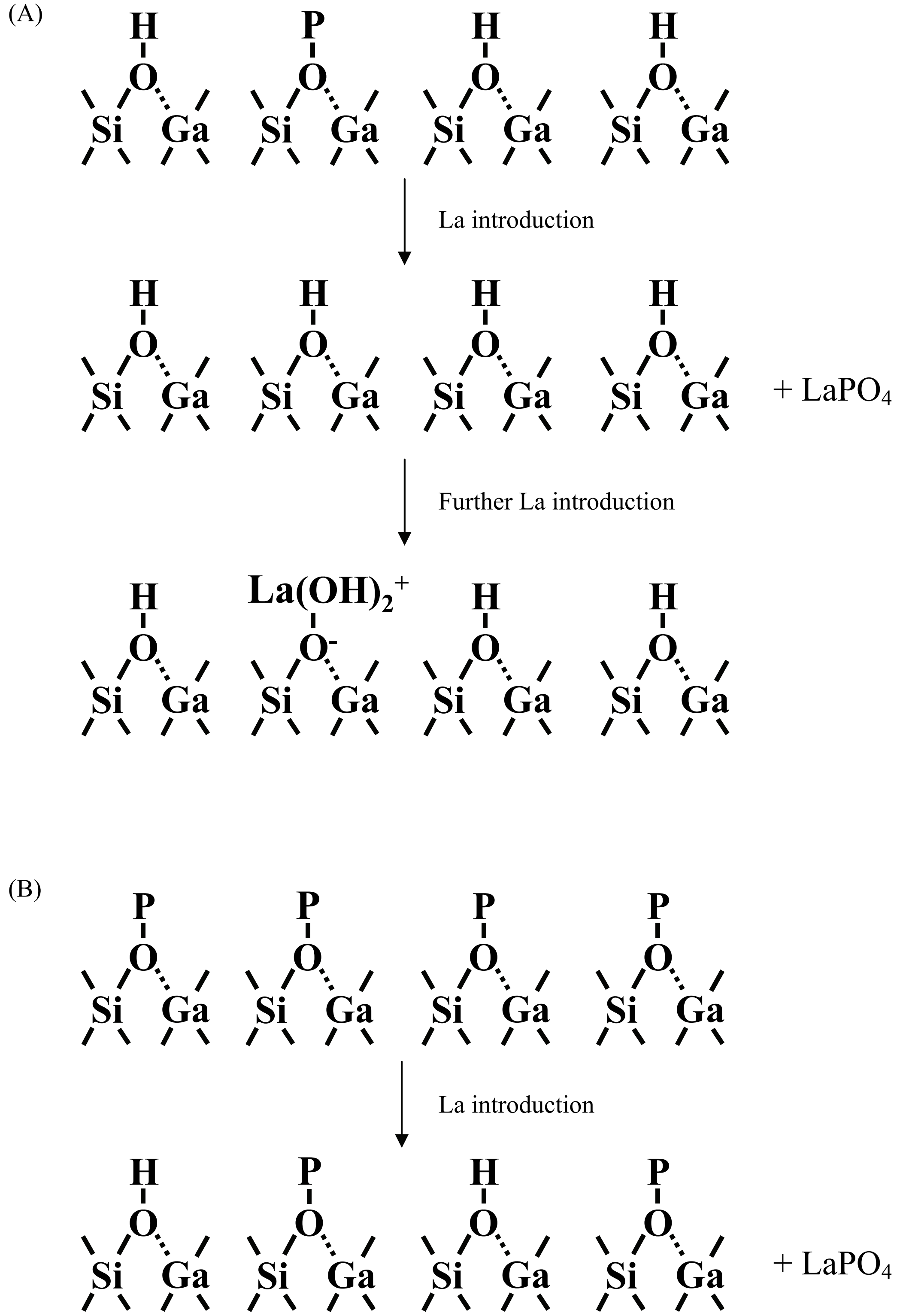

Figure 9 Change in the structure of modified acid sites during introduction of La into P/HZSM-5(Ga) with P/Ga ratios of (A) 0.2 and (B) 1.0.

P: Phosphorous species interacting with Brønsted acid sites.

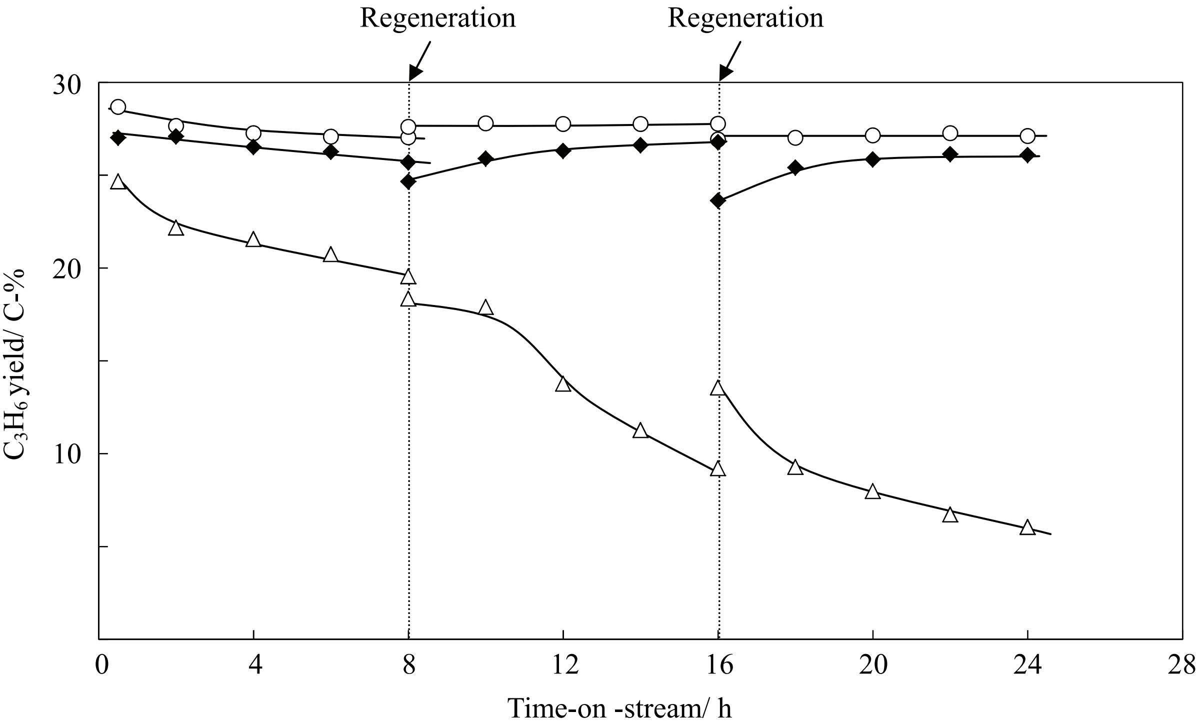

Figure 10 Time-on-stream of C_3H_6 yield for ethanol conversion over (△) HZSM-5(Ga), (◆) P/HZSM-5(Ga) with P/Ga ratio of 0.2, and (○) La/P/HZSM-5(Ga) with P/Ga ratio of 1.0 and La/Ga ratio of 0.4.

Catalysts were regenerated by calcination at 500 ˚C for 10 h in air.

Temp. = 500 ˚C, W/F = 0.02 g_{cat}/ml/min

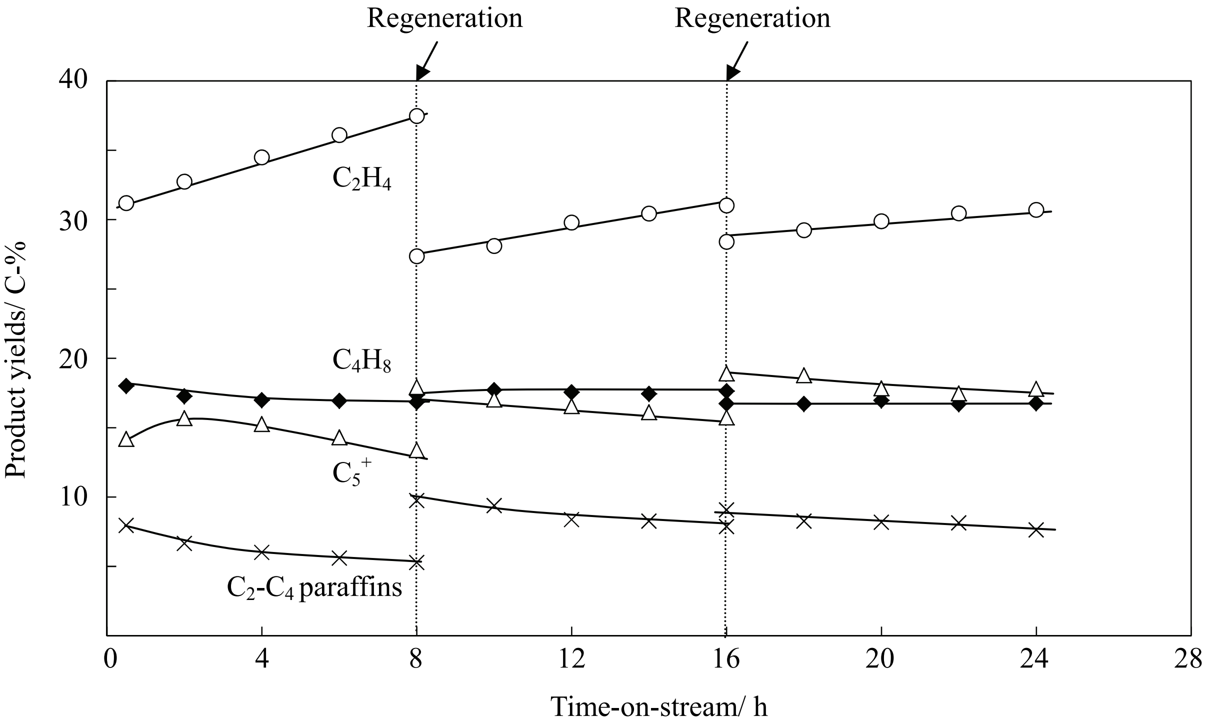

Figure 11 Time-on-stream of product yields for ethanol conversion over La/P/HZSM-5(Ga) with P/Ga ratio of 1.0 and La/Ga ratio of 0.4.

Catalysts were regenerated by calcination at 500 ˚C for 10 h in air.

Temp. = 500 ˚C, W/F = 0.02 g_{cat}/ml/min

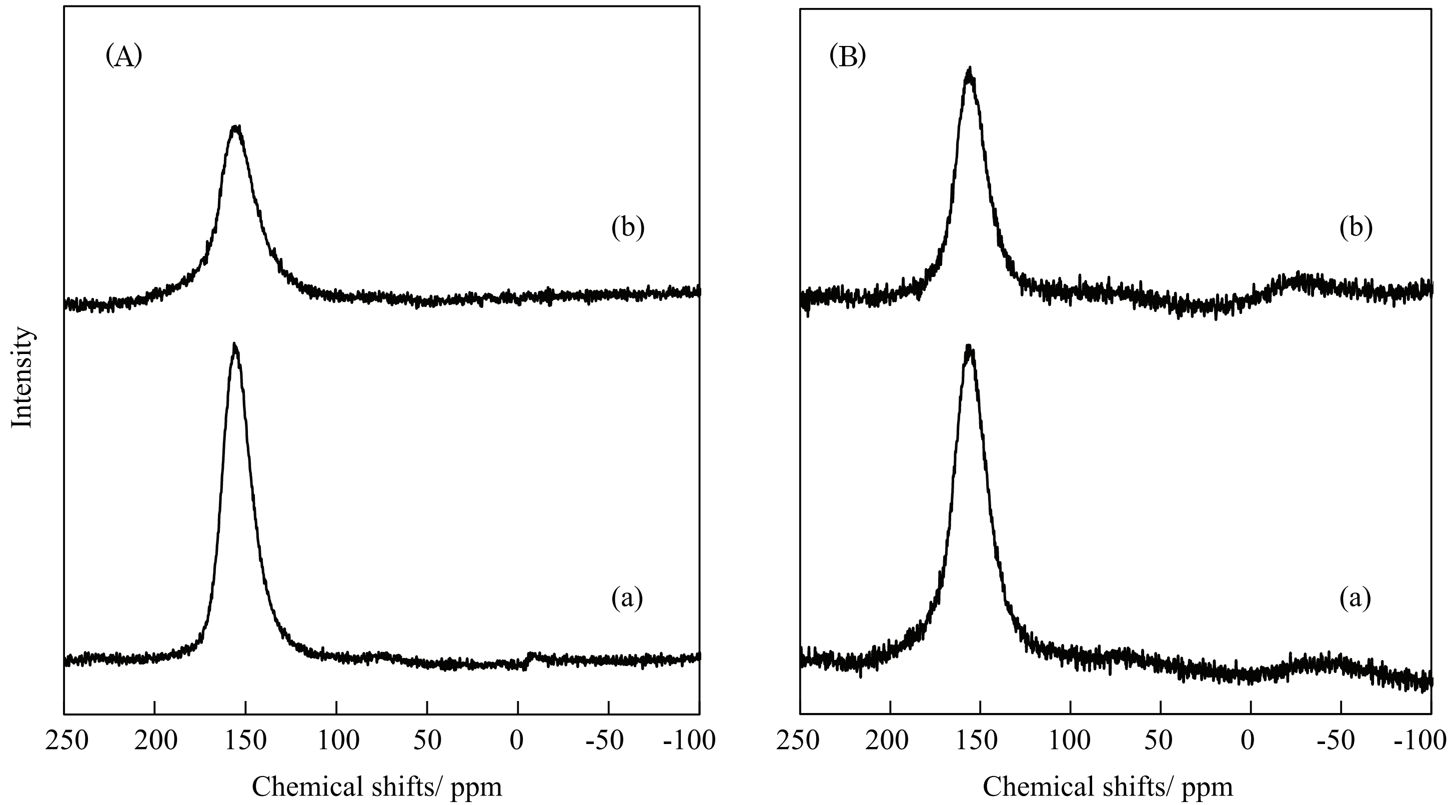

Figure 12 ^{71}Ga MAS NMR spectra of (A) HZSM-5(Ga) and (B) La/P/HZSM-5(Ga) with P/Ga ratio of 1.0 and La/Ga ratio of 0.4 (a) before and (b) after 24 h of time-on-stream.

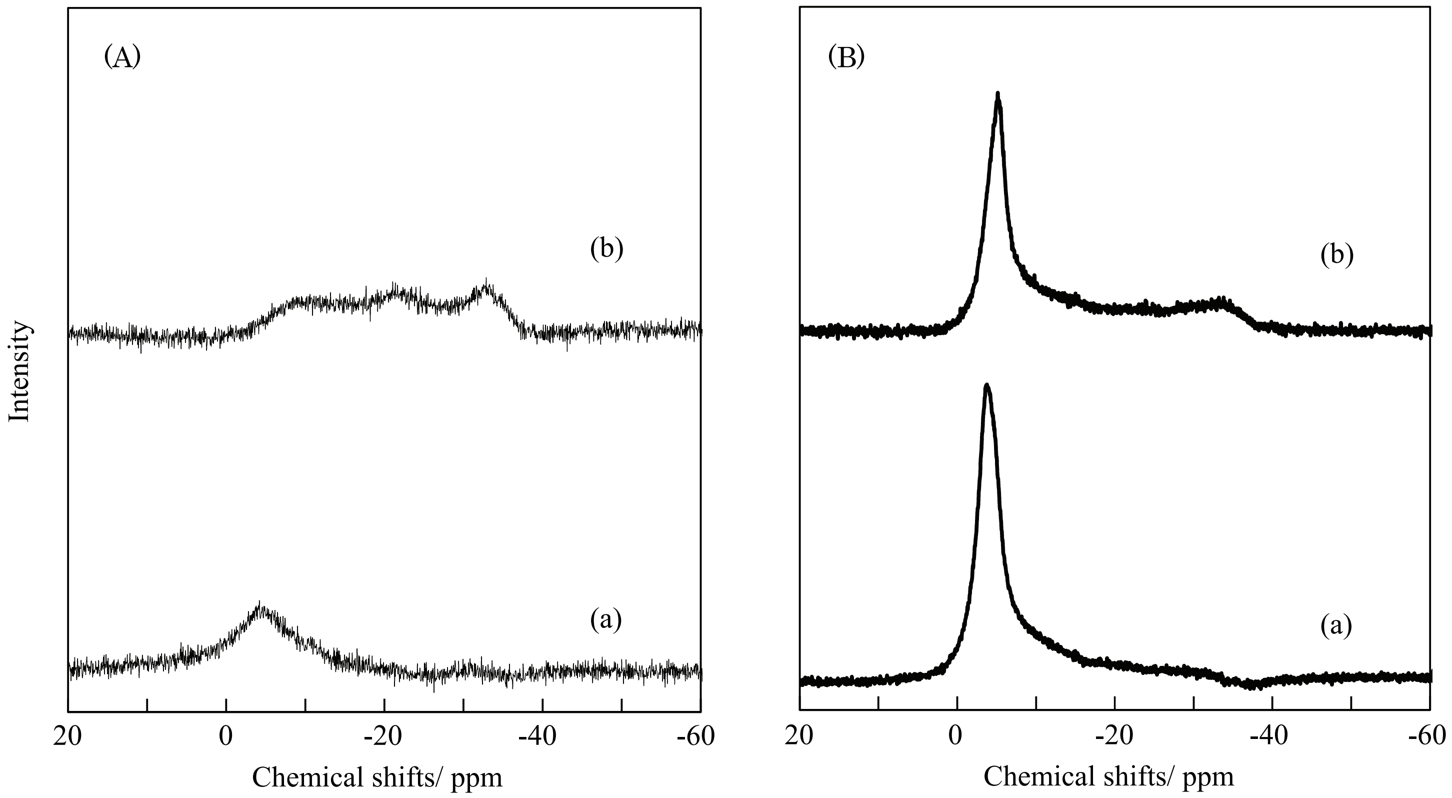

Figure 13 ^{31}P MAS NMR spectra of (A) P/HZSM-5(Ga) with P/Ga ratio of 0.2 and (B) La/P/HZSM-5(Ga) with P/Ga ratio of 1.0 and La/Ga ratio of 0.4 (a) before and (b) after of 24 h of time-on-stream.