



Photoluminescence of propylene adsorbed on γ -Ga₂O₃-Al₂O₃ solid solutions in relation to their catalysis for CH₄-SCR of NO

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ABSTRACT

When a solvothermally prepared γ -Ga₂O₃-Al₂O₃ (Ga 30 mol%) catalyst was treated with C₃H₆ followed by heating at 523 K, it colored yellow [J. Catal. 259 (2008) 36]. The photoluminescence (PL) spectra of the colored species showed two bands at near ultraviolet (383 nm) and blue-green (487 nm) regions under excitation at 343 nm, and a blue-green band (491 nm) under excitation at 436 nm. The former emissions were attributed to the carbenium ions on the tetrahedral Ga³⁺ sites in γ -Ga₂O₃-Al₂O₃, and the latter, to those on the octahedral Ga³⁺ sites. The band intensity at 383 nm increased by heating the C₃H₆-loaded catalyst upto 523 K and further increase in temperature decreased the band intensity. The intensity of the emission band at 383 nm linearly correlated with the catalytic activity of γ -Ga₂O₃-Al₂O₃ for selective catalytic reduction of NO with CH₄.

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1. Introduction

The Ga₂O₃-Al₂O₃ catalysts have high activities for selective catalytic reduction (SCR) of NO with hydrocarbons [1–5]. Active sites of these catalysts were elucidated to be tetrahedral Ga³⁺ ions having octahedral Al³⁺ ions in the next nearest neighbor sites. However, we have reported that the γ -Ga₂O₃-Al₂O₃ catalysts prepared solvothermally in a variety of media exhibited various activities depending on the media used, although the catalysts have the same content of Ga³⁺ ions entirely located in the available tetrahedral sites of the spinel structure [4–6]. We have reported that UV–vis spectra of C₃H₆ adsorbed on γ -Ga₂O₃-Al₂O₃ as a probe are closely related to the catalytic activity [6]: Two absorption bands were observed at 340 and 430 nm. The former band was assigned to C₃H₆ adsorbed on tetrahedral Ga³⁺ sites, while the latter band, to C₃H₆ adsorbed on octahedral Ga³⁺ sites [6]. The larger the intensity of the former band is, the higher the catalytic activity of γ -Ga₂O₃-Al₂O₃ for CH₄-SCR is.

It was reported that β -Ga₂O₃ nanobelt prepared by a thermal evaporation method from a mixture of gallium metal and SiO₂ afforded photoluminescence (PL) centered at 330 and 450 nm under 325 nm irradiation [7]. No PL emission, however, was observed from the γ -Ga₂O₃-Al₂O₃ solid solutions themselves

heated at 523–923 K in O₂ or in vacuo. When C₃H₆-loaded γ -Ga₂O₃-Al₂O₃ catalyst was heated at 523 K or above, it colored yellow, and irradiation of the colored catalyst with a light at 343 nm or 436 nm gave PL: The former irradiation afforded emissions centered at 383 and 487 nm, and the latter, at 491 nm. The yellow-colored species derived from C₃H₆ by adsorption on γ -Ga₂O₃-Al₂O₃ was assigned to carbenium ions [6]. In this paper, we have investigated PL emission and excitation of the yellow-colored species on γ -Ga₂O₃-Al₂O₃ in relation to the catalytic activity for CH₄-SCR of NO.

2. Experimental

2.1. Preparation of γ -Ga₂O₃-Al₂O₃ solid solutions by a solvothermal method

γ -Ga₂O₃-Al₂O₃ solid solutions were prepared by a solvothermal method [8,9] in the following manner: A mixture of gallium acetylacetonate (Mitsuwa Chemical Co. Ltd.; 2.00 g) and aluminum triisopropoxide (Nacalai Tesque Co. Ltd.; 2.60 g) was suspended in 80 ml of a reaction medium (ethylene glycol (EG), 2-methylaminoethanol (MAE), 1,5-pentanediol (1,5PG), diethylenetriamine (dEtA)) in a test tube, and the tube was placed in a 200-ml autoclave [10]. Thirty milliliters of the same reaction medium was placed in the gap between the autoclave wall and the test tube. After the air in the autoclave was completely replaced with N₂, the reaction mixture was heated to 573 K at a rate of 2.5 K/min, kept at the temperature for 2 h, and then cooled to room temperature. The

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product was repeatedly washed with acetone by vigorous mixing and centrifuging, and then air-dried. The solid solution was calcined at 973 K in air for 30 min to give a γ -Ga₂O₃-Al₂O₃ catalyst. The solid solutions will be designated as γ -Ga₂O₃-Al₂O₃ (A, *x*), where A is the medium used for solvothermal synthesis and *x* is the Ga₂O₃ content in the solid solution. For example, γ -Ga₂O₃-Al₂O₃ (dEtA, 0.3) means γ -type defective spinel with the Ga₂O₃ content of 30 mol% solvothermally prepared in diethylenetriamine.

Two spinel oxides, MgGa₂O₄ and ZnGa₂O₄ were prepared by a glycothermal method in 1,5-pentandiol from magnesium and gallium acetylacetonates and zinc and gallium acetylacetonates, respectively [10,11].

HNa-Y-zeolite (reference catalyst, JRC-Z-HY5.5; 68% H⁺ ion exchanged) was supplied from Catalysis Society of Japan.

2.2. Photoluminescence of C₃H₆ adsorbed on Ga₂O₃-Al₂O₃ solid solutions

One hundred milligrams of finely powdered Ga₂O₃-Al₂O₃ was placed in a 5 mm quartz tube, followed by evacuation and heating to 473 K. When the temperature reached 473 K, oxygen (13.3 kPa) was charged and the tube was heated to 923 K where oxygen was evacuated once again; then, fresh O₂ (20 kPa) was again charged. The tube was kept at that temperature for 1 h, followed by cooling to room temperature and evacuation. Propylene (4 kPa) was charged at 293 K followed by heating to 523 K (473–673 K) for 15 min. Propylene-treated γ -Ga₂O₃-Al₂O₃ colored light yellow. The color became deep with the rise of temperature and turned brown above 623 K. PL excitation and emission measurements were carried out with a Shimadzu RF-5300 PC photoluminescence spectrometer at room temperature in the presence of C₃H₆. Note, however, that no change was observed in the PL spectra when spectra were taken after evacuation of C₃H₆. Although PL emission and excitation spectra were recorded with high or low sensitivity, and with band widths (excitation and emission) of 1.5–3 nm, each PL emission spectrum was calibrated to the spectrum measured under the condition of 3 nm excitation and 1.5 nm emission band widths in order to compare the emissions with intensity difference by three orders of magnitude. Although calibration was carried out quantitatively, the recorded PL intensity is not necessarily quantitative since the quantity of a sample corresponding to the irradiated area is varied from experiment to experiment because of difference in bulk density of the samples. However, the deviation of bulk densities among the samples was within $\pm 10\%$.

3. Results and discussion

3.1. PL spectra of propylene adsorbed on γ -Ga₂O₃-Al₂O₃ solid solutions

When propylene was adsorbed on γ -Ga₂O₃-Al₂O₃ (dEtA, 0.3) followed by heating at 523 K for 15 min, it colored light yellow [6]. PL emission and excitation spectra of C₃H₆ adsorbed on γ -Ga₂O₃-Al₂O₃ are shown in Fig. 1. Since no change of the spectra was observed after evacuation of C₃H₆, PL measurements spectra were taken in the presence of C₃H₆ unless otherwise stated. When C₃H₆ adsorbed on γ -Ga₂O₃-Al₂O₃ was irradiated with 343 nm light, PL emissions centered at 383 and 487 nm were observed (Fig. 1). The intensity of the former is larger than that of the latter. When it was excited by 436 nm light, the emission at 491 nm was observed (Fig. 1). When the received light was set at 380 nm, the PL excitation showed a peak at 350 nm (Fig. 1(c)). Two excitation maxima were observed at 347 and 452 nm when the received light was 500 nm (Fig. 1(d)). The excitation wavelengths coincide with the absorption

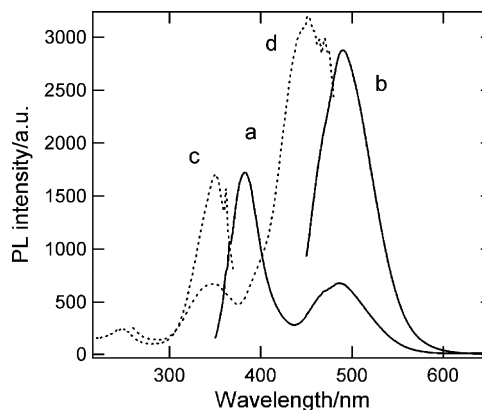


Fig. 1. PL emission (solid line) and excitation spectra (broken line) of C₃H₆ adsorbed on γ -Ga₂O₃-Al₂O₃ (dEtA, 0.3) heated at 523 K. Emission spectra a: λ_{ex} 343 nm, b: λ_{ex} 436 nm. Excitation spectra, received light: c: 380 nm, d: 500 nm.

bands in the UV-vis spectra of C₃H₆ adsorbed on γ -Ga₂O₃-Al₂O₃ [6].

No PL emission was observed for C₃H₆ adsorbed on pure γ -Al₂O₃. However, when C₃H₆-loaded γ -Ga₂O₃ (dEtA, 1.0) was heated at 523 K, the sample colored yellow and caused weak PL emission (502 and 530 nm) under excitation with 436 nm. These results indicate that PL is originated from C₃H₆ adsorbed on the Ga³⁺ sites.

PL emission spectra of C₃H₆ adsorbed on two spinel compounds, MgGa₂O₄ and ZnGa₂O₄, are shown in Fig. 2. ZnGa₂O₄ is a normal spinel in which all of Ga³⁺ ions are located in the octahedral sites [11]. On the other hand, MgGa₂O₄ is an intermediate spinel where available tetrahedral sites are occupied by Mg²⁺ and Ga³⁺ ions [12].

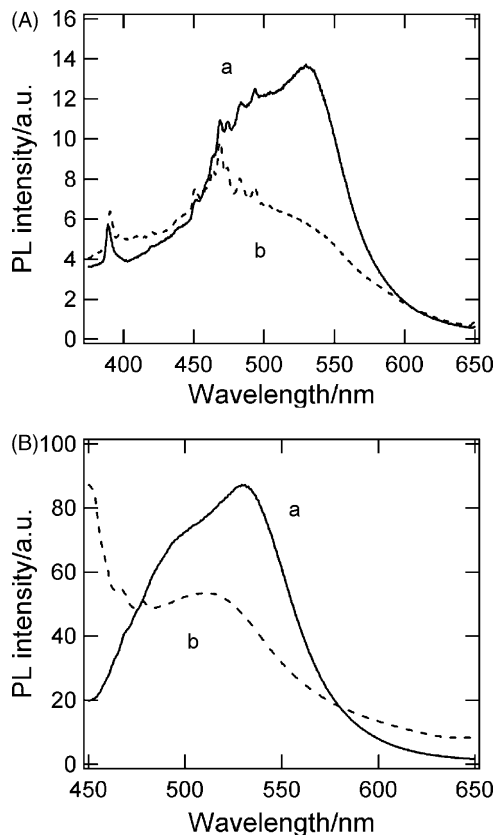


Fig. 2. PL emission spectra of C₃H₆ adsorbed on MgGa₂O₄ and ZnGa₂O₄ heated at 573 K. (A): MgGa₂O₄: a: λ_{ex} 343 nm, (B) λ_{ex} 436 nm, b: ZnGa₂O₄: a: λ_{ex} 338 nm, b: λ_{ex} 450 nm.

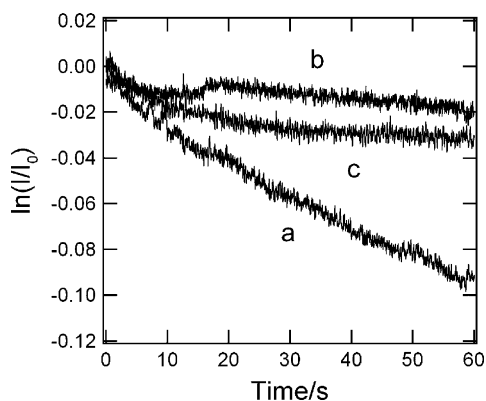


Fig. 3. Plots of time decay for the PL emission during PL measurement of adsorbed C_3H_6 on $\gamma\text{-Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ (dEtA, 0.3). a: λ_{ex} 343 nm, λ_{em} 385 nm, b: λ_{ex} 343 nm, λ_{em} 500 nm, c: λ_{ex} 436 nm, λ_{em} 500 nm.

No emission at 380 nm was observed, but weak PL emissions at ~ 500 and 530 nm were obtained from MgGa_2O_4 with the excitation of lights at 343 and 436 nm, respectively. On the other hand, ZnGa_2O_4 gave PL emission at 480 and 510 nm with the excitation lights at 338 and 450 nm, respectively. Although these intensities are low, propylene can be activated by gallium ions at 473 K and above to give PL.

PL emissions at 383 and 487 nm excited by 343 nm light are derived from carbenium ions on tetrahedral Ga^{3+} sites in $\gamma\text{-Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$, while the emission at 491 nm excited by 436 nm light is derived from carbenium ions on octahedral Ga^{3+} sites [6]. Since Ga_2O_3 , MgGa_2O_4 and ZnGa_2O_4 gave only weak PL emissions, we can conclude that PL emission is greatly enhanced by $\text{Ga}^{3+}\text{-O-Al}^{3+}$ linkage.

Fig. 3 shows the decay of emission at 380 nm (λ_{ex} : 343 nm), 500 nm (λ_{ex} : 343 nm) and 500 nm (λ_{ex} : 436 nm) at 293 K. The first-order rate constant for the disappearance of the species emitting 380 nm light is estimated to be $1.3 \times 10^{-3} \text{ s}^{-1}$ under irradiation of 343 nm light of the spectrometer. Two emissions at 500 nm from the excitation at 343 and 436 nm were slowly diminished during the illumination at 293 K. The emission intensities were also decreased with the elapse of time without illumination: when C_3H_6 -loaded sample sealed in a quartz tube was allowed to stand at room temperature for 5 months, the emission intensities at 383 nm (λ_{ex} : 343 nm), at 487 nm (λ_{ex} : 343 nm), and at 500 nm (λ_{ex} : 436 nm) were decreased by a half, 2/3 and 0.85, respectively. The difference in the decay of these emissions shows that two emissions caused by the excitation with the 343 nm light are derived from two different species. Because the expansion of the conjugation system of the adsorbed species causes the higher wavelength shift of the absorption, these two emissions seem to be due to the same C_3H_6 species adsorbed on different kinds of Ga^{3+} species.

Exposure of the C_3H_6 -loaded sample to O_2 caused no change in PL spectra. However, the addition of water lost yellow color and ceased PL emission.

3.2. Effects of heating temperatures on the PL characteristics

When C_3H_6 -loaded $\gamma\text{-Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ was heated at 473 K for 15 min, the PL emission at 383 nm clearly appeared by excitation at 343 nm, but no emission at 487 nm was observed as shown in Fig. 4(A)-a. Since almost no coloration was observed, the emission at around 500 nm under excitation at 436 nm was weak (Fig. 4(B)-a). The emission at 380 nm became the strongest after heating at 523 K where the sample turned light yellow. At the same time, the emission at 500 nm began to appear. Further heating at 573 K decreased the intensities of both the emissions and concomitantly caused the

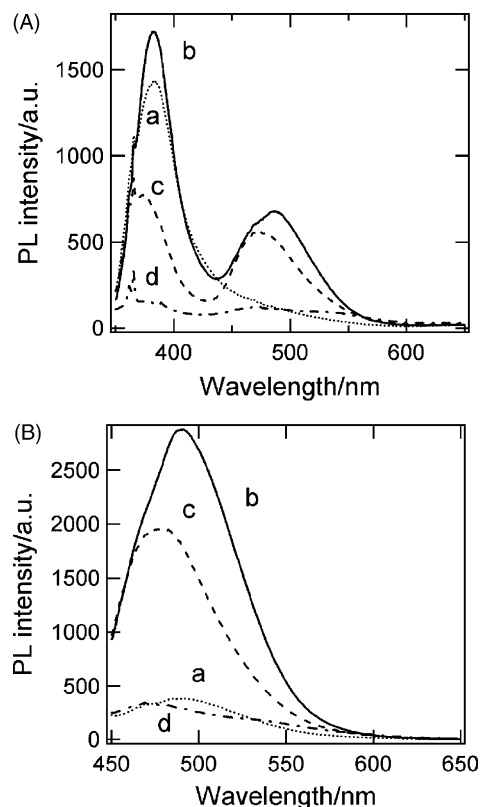


Fig. 4. Effects of heating temperatures on the PL emission of C_3H_6 adsorbed on $\gamma\text{-Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ (dEtA, 0.3). (A): λ_{ex} 343 nm, (B): λ_{ex} 436 nm, a: 473 K, b: 523 K, c: 573 K, d: 623 K.

shift of emission peaks into lower wavelengths. One possible explanation for these changes might be that the bonds between gallium and carbenium ions are strengthened by heating. Adsorbed C_3H_6 turned brown by heating at 623 K and intensities of the emissions largely decreased. Almost similar tendency was observed in the PL emission spectra excited by 436 nm light. Further heating at 673 K resulted in coloring deep brown and PL emissions were completely ceased.

3.3. Effects of Ga_2O_3 contents in $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ on the PL characteristics

PL emission spectra of C_3H_6 -loaded $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ (dEtA, 0.15, 0.30 and 0.75) heated at 523 K are shown in Fig. 5. Emission peak intensities of C_3H_6 adsorbed on 30 mol% $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ are larger than those of C_3H_6 adsorbed on 15 and 75 mol% $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ for both excitations at 343 and 436 nm. PL emission intensities of C_3H_6 adsorbed on $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ after heating at 473, 523 and 573 K are summarized in Fig. 6. For C_3H_6 adsorbed on 30 mol% $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$, PL emissions with excitation wavelengths of 343 and 436 nm became the most intense by heating at 523 K. On the other hand, PL emission of C_3H_6 adsorbed on 15 mol% $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ was greatly enhanced by heating at 573 K. Very weak PL was emitted from C_3H_6 adsorbed on 75 mol% $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ even by heating at 573 K.

The activities of the $\gamma\text{-Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ catalysts with 30 mol% Ga_2O_3 content which were solvothermally prepared in different solvents (NO conversion at 773 K: ethylene glycol, 1.8%; 2-methylaminoethanol, 24%; 1,5-pentanediol, 46%; diethylenetriamine, 96% [6]) depended on the solvent used for the solvothermal synthesis in spite of their nearly equal Ga^{3+} compositions at the tetrahedral sites [6]. Fig. 7 shows the PL intensities of C_3H_6 adsorbed on the above-mentioned $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ solid solutions. The data for

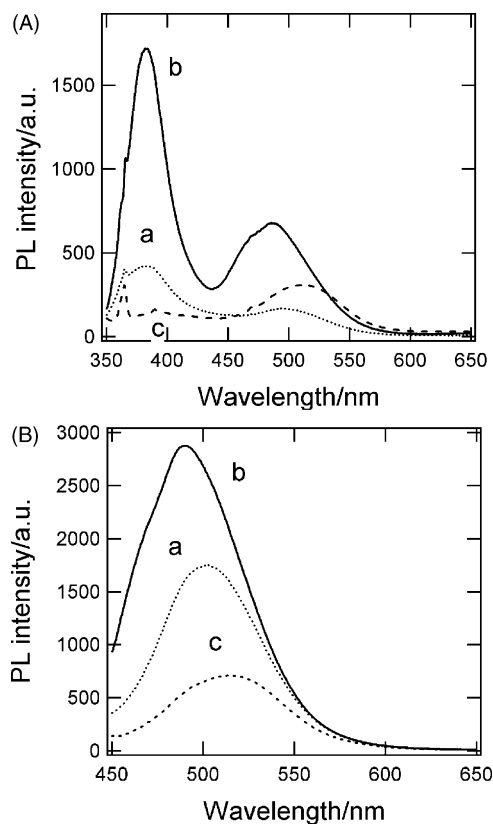


Fig. 5. Effects of Ga_2O_3 contents on the PL intensities of adsorbed C_3H_6 heated at 523 K. (A): λ_{ex} 343 nm, (B): λ_{ex} 436 nm, $\text{Ga}_2\text{O}_3/\text{Al}_2\text{O}_3$ ratio: a: 15/85, b: 30/70, c: 75/25.

$\gamma\text{-Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ (EG, 0.3) are not incorporated in the figure because of very low PL intensities. High PL intensities are derived from the C_3H_6 -treated solid solution that exhibited high UV–vis absorption intensities at 340 nm and 430 nm [6].

Fig. 8 shows the plots of the catalytic activity for $\text{CH}_4\text{-SCR}$ of NO against the intensity of emission at 383 nm with excitation at 343 nm (the sample was heated at 523 K after adsorption of C_3H_6). Two NO conversions are taken in Fig. 8: steady-state conversion at 773 K and initial NO conversion at 673 K [6]. The former NO conversion fits in a straight line, but the latter one gives a curved plot. The $\gamma\text{-Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ catalyst on which adsorbed C_3H_6 strongly emitted at 380 nm with the excitation light of 343 nm has high activity for SCR-NO with CH_4 . We have observed no relationship between catalytic activity and the PL emission intensities at 480–500 nm excited by 343 and 463 nm light. Since the 487 nm emission required higher temperature than that required by the 383 nm emission, the Ga^{3+} sites involved in the former emission are thought to be less active than those related with the latter emission. The results shown in Fig. 8 indicate that the catalytic activity in $\text{CH}_4\text{-SCR}$ of NO can be assessed by the intensity of PL emission at 383 nm, as was the case for the absorption at 340 nm in the UV–vis spectra of C_3H_6 adsorbed on tetrahedral Ga^{3+} sites [6].

3.4. Active species of the PL emission

Mixed oxides of $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ are known to have weak acidities [13–17]. Solvothermally prepared $\gamma\text{-Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ catalyzed isomerization of 1-butene at 323 K and above [18]. The initial cis/trans ratio of 2-butene is close to unity, suggesting that the carbenium ions interacted with Ga ions are formed as intermediates. Thermal treatment of C_3H_6 adsorbed on $\gamma\text{-Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ at above 523 K resulted in coloring yellow. The absorption bands at 340 and 430 nm

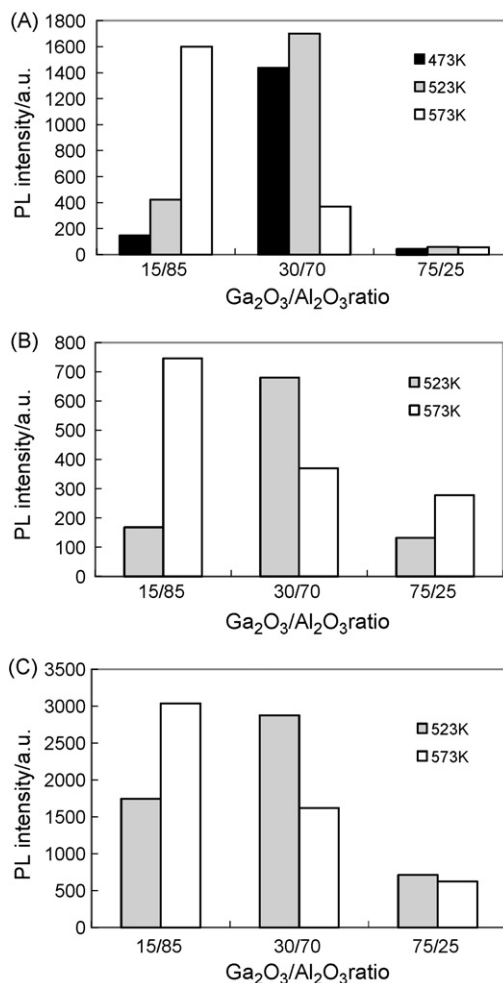


Fig. 6. Effects of Ga_2O_3 content in $\gamma\text{-Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$ and heating temperature on the PL emission intensities. (A): λ_{ex} 343 nm, λ_{em} 380 nm, (B): λ_{ex} 343 nm, λ_{em} 480–500 nm, (C): λ_{ex} 436 nm, λ_{em} 480–500 nm.

were assigned to the carbenium ions formed on weakly acidic tetrahedral and octahedral Ga^{3+} sites, respectively [6]. Carbenium cations are well known to be formed by the reactions of olefins with H-zeolites [19]. Forster and Kiricsi reported that C_3H_6 adsorbed on HNa-Y-zeolite (72% H^+ ion exchanged) afforded absorption bands at 309, 380 and 470 nm depending on heating temperature. These bands are assigned to allyl, dienyl, and trienyl carbenium ions, respectively [20]. The positions of absorption bands depend on H^+ ion-exchange degree of HNa-Y-zeolite [19].

PL emissions of C_3H_6 adsorbed on HNa-Y-zeolite (68% H^+ ion exchanged) heated at 473–573 K were examined (Fig. 9). It gave emission bands at 349 and 360 nm with excitation at 300 nm light; however, no emission band at around 500 nm was observed. The intensity of emission excited by 300 nm light was larger than that excited by 343 nm light (the latter wavelength gave strong emissions for the C_3H_6 -loaded $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$). The emission intensity became a maximum at the heating temperature of 523 K. The emission peak with excitation of 436 nm light shifted from 550 nm to 470 nm by the increase in heating temperature from 473 to 573 K. The large difference in the wavelength of the emissions suggests that thermal treatment changed the structure of emission sources.

UV–vis spectra of C_3H_6 adsorbed on HNa-Y-zeolite indicated that allyl cations react with further C_3H_6 yielding dienyl and trienyl carbenium ions in the course of heat treatment [19–22]. The absorption band shifts to higher wavelength by 60–80 nm by the increment of every $[-\text{CH}=\text{CH}-]$ unit in carbenium ions accord-

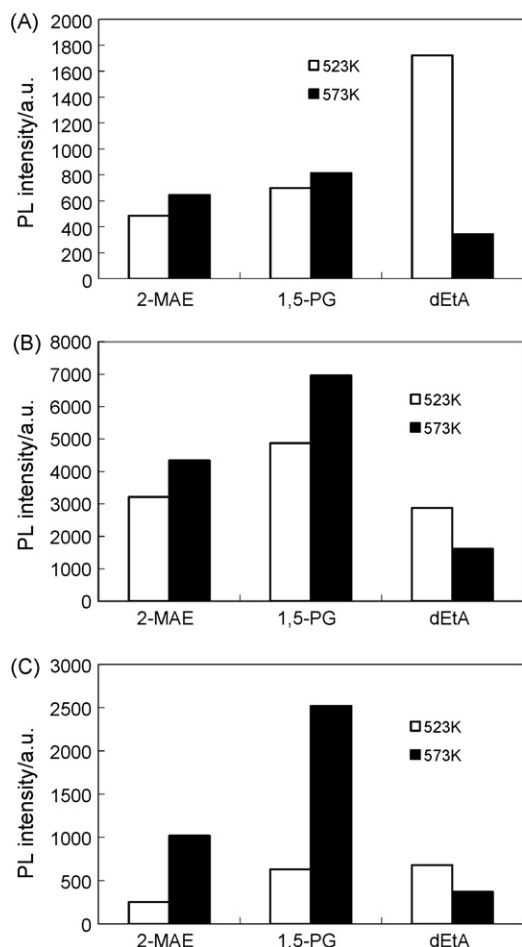


Fig. 7. PL intensities of C_3H_6 adsorbed on $Ga_2O_3-Al_2O_3$ (0.3) prepared solvothermally in various solvents. (A): λ_{ex} 343 nm, λ_{em} 380 nm, (B): λ_{ex} 343 nm, λ_{em} 480–500 nm, (C): λ_{ex} 436 nm, λ_{em} 500 nm. MAE: 2-methylaminoethanol, 1,5PG: 1,5-pentandiol, dEtA: diethylenetriamine. The sample was heated at the temperature specified in the figure after adsorption of C_3H_6 .

ing to the empirical correlation [18–21]. On the other hand, no further absorption bands other than 340 and 430 nm bands have been observed for C_3H_6 adsorbed on $\gamma-Ga_2O_3-Al_2O_3$ by heating. Carbenium ions are formed from the reactions between olefins and acid sites of catalysts [19]. There is a distribution in acid strength of most solid acid catalysts. The acidity of $\gamma-Ga_2O_3-Al_2O_3$ is moderate and acid site density in the surface is rather low [5]. Two emissions

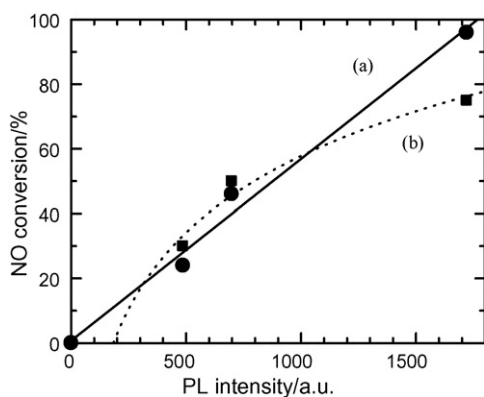


Fig. 8. Relationship between NO conversion in CH_4 -SCR of NO and PL emission intensity (λ_{ex} 343 nm, λ_{em} 380 nm; the sample was heated at 523K after adsorption of C_3H_6). (a): steady-state conversion at 773 K, (b): initial conversion at 673 K.

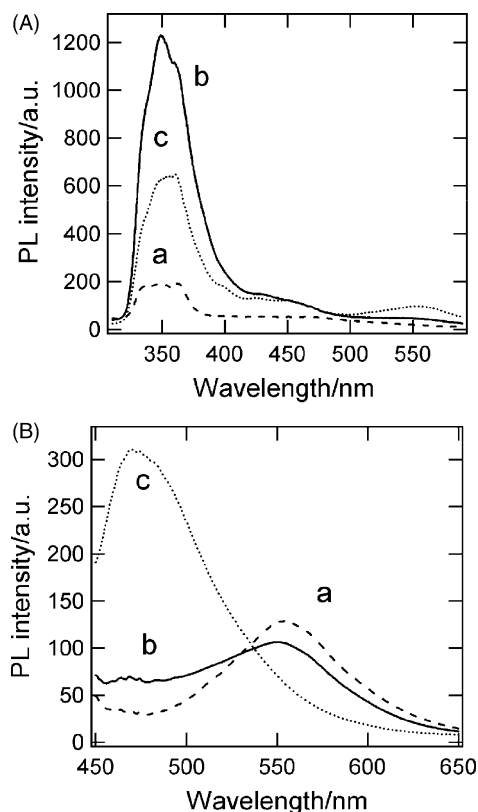


Fig. 9. PL emission spectra of C_3H_6 adsorbed on HNa-Y-zeolite. (A): λ_{ex} 300 nm, (B): λ_{ex} 436 nm. Heating temperature, a: 473 K, b: 523 K, c: 573 K.

at 383 and 487 nm caused by the excitation with 343 nm light seem to be derived from carbenium ions adsorbed on Ga^{3+} sites having different acid strength. The latter emission appeared at higher heating temperature than the former emission did. The verification has been pursued by the MO calculation.

4. Conclusion

Propylene was allowed to react with weak acid sites of $\gamma-Ga_2O_3-Al_2O_3$ solid solutions at 473 K and above to give yellow carbenium ions. Photoluminescence (PL) emission showed near ultraviolet and blue-green bands at 383 and 487 nm under excitation with 343 nm. Another emission was observed at 491 nm under excitation with 436 nm. Three emission intensities changed with the heating temperature. The band intensity at 383 nm became a maximum by heating the adsorbed C_3H_6 at 523 K and then decreased by further heating. PL emissions at 383 and 487 nm suggest the existence of more than one species. The emission band intensity at 383 nm was closely correlated with the catalytic activity of $\gamma-Ga_2O_3-Al_2O_3$ solid solutions for CH_4 -SCR of NO. The PL emitting species persisted at room temperature for months in C_3H_6 or O_2 , but the PL emission ceased with contact with water. This is a case that PL spectroscopy can afford more information on the surface species than UV-vis one.

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