Thermally stable alumina–gallia aerogel as a catalyst for NO reduction with C_3H_6 in the presence of excess oxygen

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In order to improve thermal stability, an alumina–gallia aerogel was prepared and the catalyst performance for NO reduction with C_3H_6 was compared with that of an alumina–gallia xerogel. Basically, both were prepared by a sol–gel method with supercritical drying for the former, while with oven drying for the latter. Upon heating at 800, 900, and 1000 °C, the aerogel exhibited higher NO conversion than the xerogel at reaction temperature <400 °C, while NO conversion was lower on the former than on the latter at >500 °C. At 450 °C, NO conversion was almost the same for these two catalysts. A marked difference was observed upon heating them at 1100 °C: the aerogel still maintained quite a high activity, while the xerogel greatly lost it. After heating the aerogel at 1100 °C, γ-phase alumina remained untransformed with its surface area of 80 m^2/g, while the xerogel was completely transformed to α-alumina with its surface area of 6 m^2/g. The high activity remaining on the aerogel heated at 1100 °C was ascribed to its large surface area.

KEY WORDS: alumina–gallia; aerogel; xerogel; selective NO reduction with C_3H_6; thermal stability

1. Introduction

Much attention has been paid to the development of catalysts for the selective catalytic reduction (SCR) of NO with hydrocarbons in the presence of excess oxygen. This is because the SCR catalyst system will open a possible route to suppress NO emission in the atmosphere from diesel and lean-burn engines, for which a conventional three-way catalyst does not work. Although a variety of metal-cation-containing zeolites have been extensively studied as SCR catalysts [1–3], zeolite-based catalysts have a serious problem of their inferior hydrothermal stability, leading to a limitation of such catalysts for practical application. Such inferiority is reported to result from dealumination occurring at the tetrahedral Al sites, by which the zeolite structure is destroyed under hydrothermal conditions [1,3,4]. It was found that unsupported and supported metal oxides were also active for NO reduction with hydrocarbons in the presence of excess oxygen [1–3,5,6]. Among many kinds of metal-oxide-based catalysts, Ga_2O_3/Al_2O_3 was reported to exhibit a good performance in the sense that the competitive combustion of hydrocarbons with adsorbed or lattice oxygen was not so serious compared with other metal-oxide-based catalysts [7,8].

Depending on engine operation, automotive catalysts are exposed to a wide range of temperature from as low as 100 °C for warm-up to as high as 1000 °C for top-speed operation. Therefore, similar to conventional three-way catalysts, an excellent heat-tolerance is required for SCR catalysts as well as hydrothermal stability. The situation that the US regulation will impose a catalytic converter to prolong its durability period from 50 000 to 100 000 miles also stimulates us to develop a high heat-tolerant SCR catalyst. It seems, however, that attention paid to heat-tolerance is rather limited for the study on SCR catalysts reported to date.

The authors developed a sol–gel method for the preparation of an alumina aerogel with an excellent thermal stability [9,10]. Here, thermal stability was evaluated in terms of the maintenance of a large surface area after heating at elevated temperatures. Our alumina aerogel prepared by this method exhibited a large surface area of 100 m^2/g even after heating it at 1200 °C, which resulted from the θ-phase remaining untransformed to the α-phase. This preparation method may lead us to expect to obtain a heat-tolerant Ga_2O_3/Al_2O_3 catalyst. In the present study, we tried to include Ga_2O_3 in alumina aerogel to prepare a heat-tolerant Ga_2O_3/Al_2O_3 catalyst and its activity was examined toward the selective reduction of NO with C_3H_6 after heating it at various temperatures. An alumina–gallia xerogel was also prepared for comparison.

2. Experimental

2.1. Catalyst preparation

The alumina–gallia aerogel was prepared in a following fashion. Aluminum triisopropoxide (20.4 g (0.1 mol); Kanto Chemicals Inc.) was hydrolyzed with 80 ml of hot Milli-Q water (80 °C) and the resultant pseudo-boehmite precipitate and the solvent were moved into a flask followed by the addition of 10 ml of 1 N HNO_3. The precipitate was

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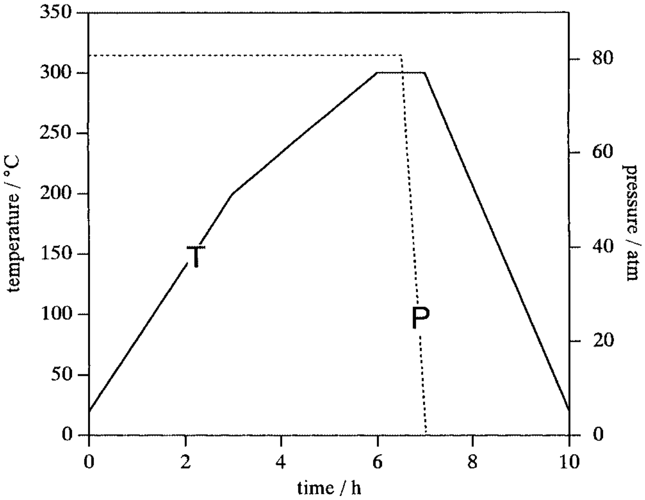

Figure 1. Temperature (T) and pressure (P) schedule.

refluxed at 90 °C for 1 h for the purpose of peptizing it to be a clear sol. Gallium(III) nitrate n-hydrate (Wako Pure Chemicals Inc.; $n = 7$–9) was dissolved in 5 ml of ethylene glycol (Wako Pure Chemicals Inc.). The amount of gallium nitrate was adjusted so that the final content was 30 wt%. The solution containing gallium nitrate and ethylene glycol was added to the clear pseudo-boehmite sol and then refluxed at 90 °C. The mixture was solidified to the gel within a few hours. After gelation, the gel was dipped into ethanol in order to remove water in the pores. This procedure was repeated three times and the amount of water was decreased to the level of reagent grade ethanol. The gel was moved into an autoclave (United Instruments Inc.) with ethanol and dried under the supercritical condition of ethanol. The temperature and pressure schedule is shown in figure 1. After supercritical drying, the prepared alumina–gallia aerogel was ground followed by heating it at 800 °C for 5 h. For preparing the alumina–gallia xerogel, the gel was moved into a beaker and dried at 110 °C overnight. After drying, the gel was ground and calcined at 800 °C for 5 h. Both the alumina–gallia aerogel and the alumina–gallia xerogel (expressed hereafter aerogel and xerogel, respectively) were further heated at 900, 1000, and 1100 °C for 5 h for the following examinations.

2.2. Characterization

XRD diffraction patterns were taken on an MXP3 powder diffractometer (MAC Science Inc.) operated at 40 kV and 20 mA with a Cu tube. BET surface area was measured by using a Belsorp36 volumetric gas adsorption instrument (Nippon Bel Inc.) at −196 °C. Pore size distribution was calculated by the D–H method [10] with the desorption branch.

2.3. NO reduction with C_3H_6

Catalyst powders were pressed to pellets and then crushed, sieved between 210 and 340 μm. 0.3 g was packed into a fixed-bed quartz glass reactor (inner diameter 8 mm) and heated in O_2 flow at 550 °C for 1 h. NO reduction was carried out with a feed mixture consisting of 668 ppm NO, 556 ppm C_3H_6, 2.5% O_2 and N_2 as a balance gas under the total pressure of 1 atm. The space velocity corresponded to 40 000 h^{-1}. The concentrations of NO and NO_2 were measured by a chemiluminescence type CLA-510ss NO_x analyzer (Horiba Inc.). Other products were analyzed with a Shimadzu 8A GC equipped with a thermal conductivity detector by using Porapak Q as a separation column.

3. Results

Under the present reaction conditions, the NO reacted was reduced almost completely to N_2 with a negligible amount of N_2O and the C_3H_6 reacted was oxidized completely to CO_2 with no formation of CO. Figures 2 and 3 illustrate catalytic activities of the aerogel and the xerogel, respectively. As shown, NO conversion increased to reach a maximum and then decreased with elevating reaction temperature. The decrease in NO conversion at higher temperatures was due to the combustion of C_3H_6 with O_2 preferable to the reduction of NO. On both the aerogel and the xerogel, NO conversion varied with the reaction temperature was quite similar between heating at 800 and 900 °C, although the temperature yielding the maximum NO conversion was lower on the former catalyst than on the latter, i.e., 400–450 °C vs. 500 °C. The maximum conversion was also lower on the aerogel than on the xerogel, i.e., 60 vs. 80%. Heating at 1000 °C resulted in a considerable decrease in NO conversion on these two catalysts, while the respective reaction temperature yielding the maximum conversion was maintained. Heating at 1100 °C caused a marked difference between the aerogel and the xerogel. On the aerogel, no further decrease in NO conversion was observed at reaction temperature >450 °C, although NO conversion slightly decreased at temperature <450 °C. On the xerogel, on the other hand, NO conversion greatly decreased in the whole range of reaction temperature and the maximum value was ca. 25%.

Figure 4 shows the XRD patterns of the aerogel heated at various temperatures. Appearing diffraction peaks were ascribed to an ill-crystallized γ-phase alumina after heating at 800 and 900 °C. In accord with the literature [8], no gallium-containing phases were observed, although the catalyst was designed to contain 30 wt% Ga_2O_3. Heating the aerogel at 1000 °C slightly improved the crystallinity of γ-phase alumina with newly formed δ-phase alumina. No gallium-containing phases were also observed. After heating the aerogel at 1100 °C, it was obvious that γ-phase alumina still remained untransformed to α-alumina.

Figure 5 shows the XRD patterns of the xerogel heated at various temperatures. Similar to the aerogel, diffraction peaks ascribable to ill-crystallized γ-phase alumina appeared after heating at 800–1000 °C. However, different from the aerogel, a complete phase transformation from γ- to α-alumina was observed after heating the xerogel at 1100 °C. No gallium-containing crystalline phases were also

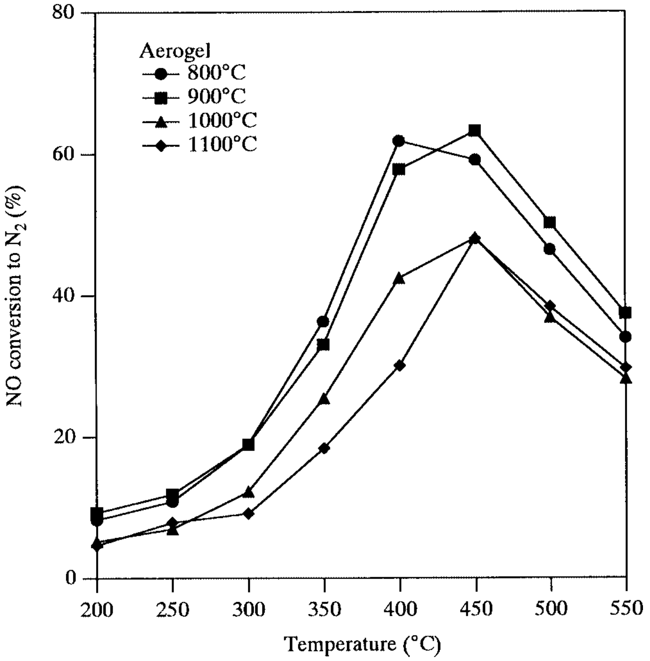

Figure 2. NO conversion to N_2 over alumina–gallia aerogel heated at various temperatures.

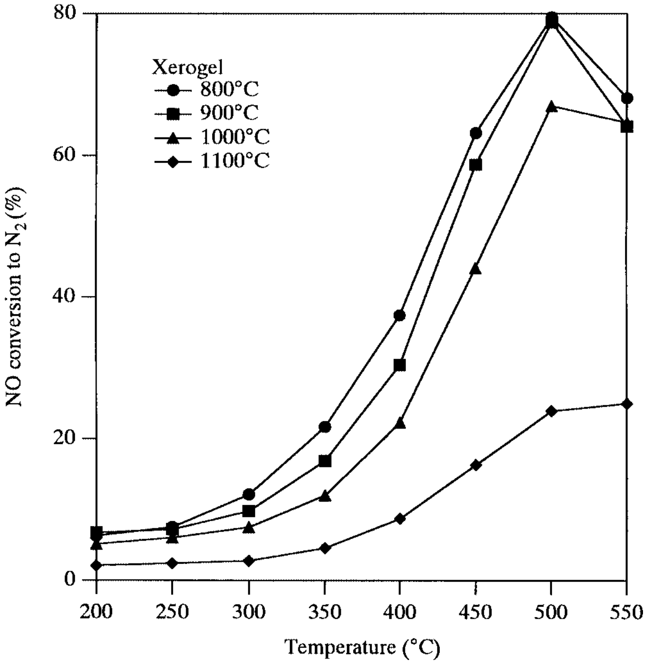

Figure 3. NO conversion to N_2 over alumina–gallia xerogel heated at various temperatures.

observed after all these heat treatments. It should, however, be noted that upon heating the xerogel at 1100 °C, each peak appeared at diffraction angles slightly lower than those corresponding to the typical α-phase alumina, resulting from a possible effect of added Ga_2O_3.

Figure 6 summarizes the specific surface areas of both the aerogel and the xerogel as a function of the heating temperature. At 800 °C, their surface areas were as large as 150 m^2/g. The surface area of the aerogel gradually decreased with the increase in heating temperature, but 90 m^2/g was maintained even after heating at 1100 °C. Similarly, the surface area of the xerogel decreased gradually to ca. 80 m^2/g with the elevation of the heating temperature up to 1000 °C. However, different from the aerogel, heating the xerogel at 1100 °C resulted in a drastic decrease in its surface area to 6 m^2/g, for which a complete phase transformation from γ- to α-alumina should be responsible.

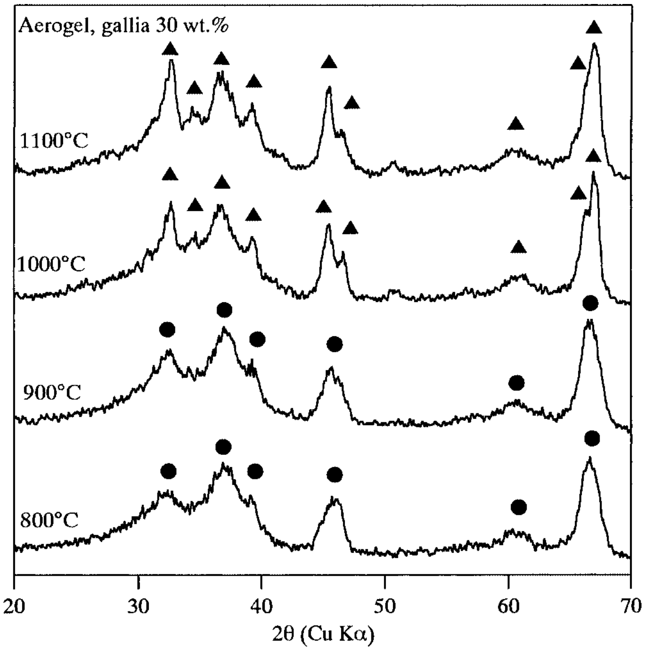

Figure 4. XRD patterns of alumina–gallia aerogel heated at various temperatures: (●) γ- and (▲) δ-phase alumina.

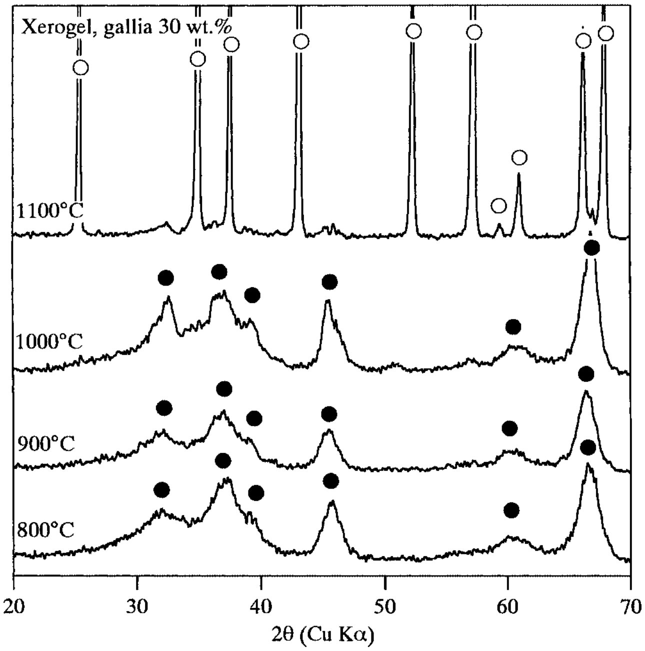

Figure 5. XRD patterns of alumina–gallia xerogel heated at various temperatures: (●) γ- and (○) α-phase alumina.

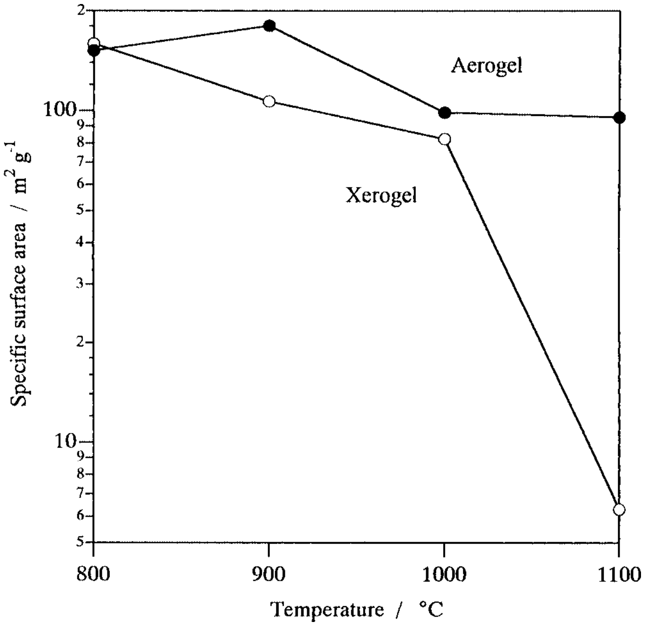

Figure 6. Specific surface area varied with the heating temperature.

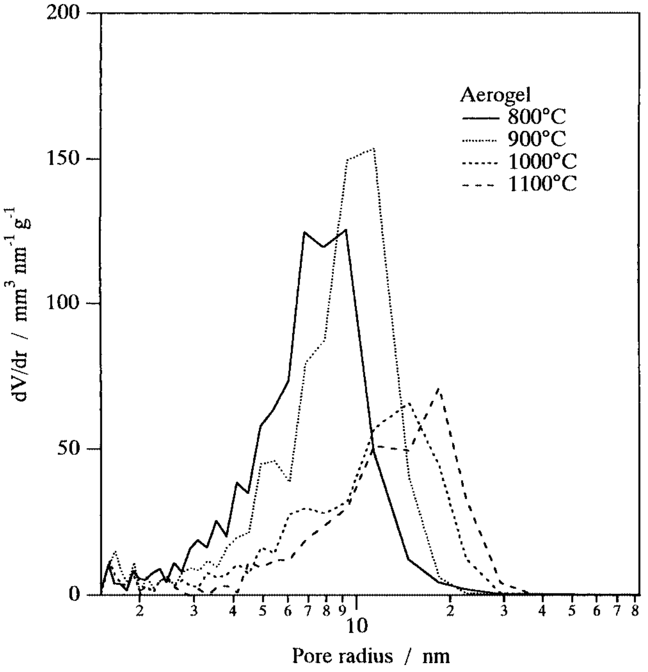

Figure 7. Pore size distribution of alumina–gallia aerogel heated at various temperatures.

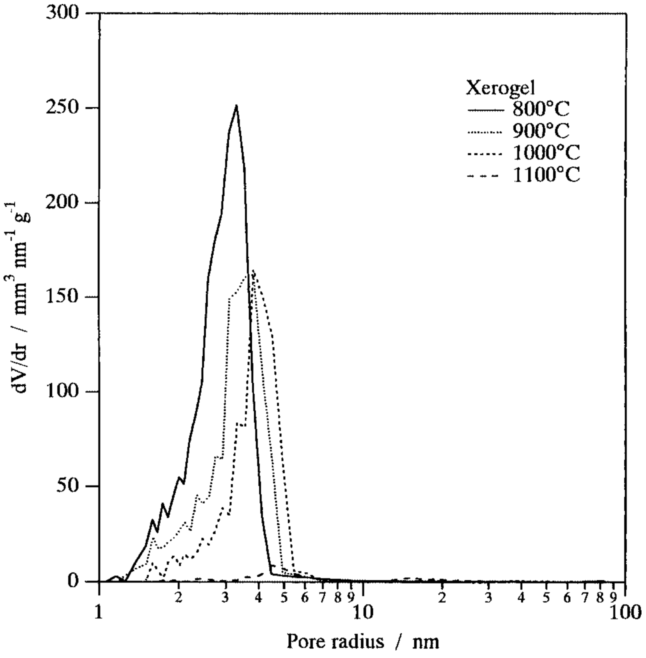

Figure 8. Pore size distribution of alumina–gallia xerogel heated at various temperatures.

Figures 7 and 8 show the pore size distributions for the aerogel and the xerogel heated at various temperatures, respectively. In case of the aerogel heated at 800 °C, the peak appeared at the pore size of about 8 nm and shifted toward a larger size with the elevation of heating temperature. The pore volume considerably decreased upon heating the aerogel at 1000 and 1100 °C. Compared with the aerogel, the pore size of the xerogel was obviously small: the peak appeared at the size of 3 nm upon heating at 800 °C. The peak of the pore size shifted to a larger side with the elevation of temperature, although the shift was more limited than that for the aerogel. Upon heating at 1100 °C, micropores almost completely disappeared from the xerogel, resulting from phase transformation to α-alumina.

4. Discussion

In our alumina–gallia system, both the aerogel and the xerogel exhibited quite a high activity for NO reduction with C_3H_6 except the xerogel heated at 1100 °C. In case of the aerogel, heating at 900 °C yielded the best catalyst performance, while the highest activity was observed upon heating the xerogel at 800 °C. The maximum NO conversion was always lower on the aerogel than on the xerogel for the comparison of the same heating temperature basis. Both the present aerogel and xerogel were prepared by a sol–gel method, by which a high dispersion of species through the formation of Ga–O–Al bonding is ensured. Haneda et al. reported the superiority of a sol–gel method for the preparation of undoped [11] and SnO_2-doped Ga_2O_3/Al_2O_3 SCR catalysts [12]. Therefore, it is natural for both our aerogel and xerogel to exhibit quite a high activity for NO reduction with C_3H_6 in the presence of excess oxygen, although the performance slightly differs from each other.

A marked difference was that after heating at 1100 °C, the aerogel was still active for NO reduction with C_3H_6 in the presence of excess O_2, while the xerogel greatly lost the activity. Upon heating at 1100 °C, the crystalline phase of the aerogel was γ-alumina but that of the xerogel was α-alumina. As a result of incomplete and complete phase transformation, the surface area differed from each other, i.e., 90 vs. 6 m^2/g, and micropores disappeared from the latter. A remaining high catalytic activity of the aerogel heated at 1100 °C should be ascribed to its maintaining a large surface area, and a very low activity of the xerogel heated at 1100 °C should be due to its small surface area. Other factors may also be responsible for the difference in catalyst performance between the aerogel and the xerogel, although the difference in surface area satisfactorily explained the result. Further study is needed.

Between our aerogel and xerogel, the drying method was only an apparent difference: supercritical drying for the former, while oven drying for the latter. We previously reported that supercritical drying was able to prepare an alumina aerogel with very low bulk density [9]. The suppression of phase transformation was also discussed in terms of the idea that the number of sites for the nucleation to α-phase alumina was decreased by lowering the bulk density [9,13]. Since the present aerogel had a low bulk density, it is considered that a close contact between particles is not easy resulting in a decrease in the number of sites for the nucleation to α-phase alumina, as discussed previously. Broader pore size distribution of the aerogel may be a result. Consequently, the phase transformation to α-alumina is suppressed, which leads to the maintenance of a large surface area even after heating at 1100 °C. Different from the aerogel, the xerogel particles contact closely with one another and as a result, the site for the nucleation to α-phase alumina is abundant in it, which leads to a ready transformation to α-alumina upon heating at 1100 °C.

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