Hydrothermal synthesis of ZnO–Ga_2O_3–Al_2O_3 spinel for NO reduction by hydrocarbon under oxygen-rich conditions

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Spinel powders with addition of ZnO into Ga_2O_3–Al_2O_3 were synthesized from a mixed solution of nitrate salts in the presence of aqueous ammonium carbonate under hydrothermal conditions at 150 °C for 48 h. The crystallization of the spinel was promoted by an increase in reaction temperature and time. This powder was studied for the selective reduction of NO with hydrocarbons (CH_4, C_2H_4, and C_3H_6) in the presence of oxygen. High durability was observed for the reduction of NO by C_2H_4 in the presence of water vapor and sulfur oxides, maintaining a high stability over 100 h.

KEY WORDS: hydrothermal; spinel type structure; hydrocarbons; NO reduction.

1. Introduction

Ga_2O_3-containing catalysts such as Ga_2O_3–Al_2O_3 with γ-Al_2O_3 phase are known to be active as a catalyst for selective reduction of NO by hydrocarbons under an oxidizing atmosphere [1]. Unfortunately, their catalytic activities are relatively low and often deteriorated by coexisting water vapor. Moreover, the γ-Al_2O_3 phase of Ga_2O_3–Al_2O_3 is well-known to have a phase transformation to α-Al_2O_3 phase around 800 °C as shown in the phase diagram of Ga_2O_3–Al_2O_3 [2]. Once the phase transformation to α-Al_2O_3 has occurred, the catalytic activity of Ga_2O_3–Al_2O_3 would almost disappear. Although the phase transformation temperature is higher than the temperature of exhaust gases, the thermal stability of Ga_2O_3–Al_2O_3 catalyst is unreliable because of the possibility for locally increasing temperature in practical use.

Chin and Hercules [3] reported that the influence of a small quantity of ZnO on the surface properties of Co-Al_2O_3 catalysts appears to be twofold. El-Shobaky *et al.* have also reported the effects of Li_2O, Na_2O and ZnO-doping on surface and catalytic properties of CuO–Al_2O_3 system. These authors claimed that ZnO-doping remarkably increased the durability of the investigated system [4]. Previous studies mentioned that zinc–alumina spinels work well for many applications because of their strong acid/base properties, high thermal stability, high mechanical resistance, and inertness to water vapor [5]. Although ZnO is sometimes regarded as member of the 3d transition metal oxide, ZnO is actually not a transition metal oxide because the 3d orbital of Zn^{2+} is filled [6]. The high selectivity of Ga_2O_3–Al_2O_3 has been originated from non-transition metal oxide i.e., non-reducing nature of gallium ion resulting in the low oxidation activity [7]. Moreover, the Zn^{2+}—O^{2-} bond seems to be very promising, since they imply that the Zn—O bond has a rather covalent nature [6]. On the other hand, the tetrahedral Ga atom also having the covalent nature, which is required to activate hydrocarbon, leading to the high activity for NO selective reduction [8]. Therefore, it has been assumed that ZnO–Ga_2O_3–Al_2O_3 with spinel phase might be interesting for the reduction of NO by hydrocarbon. It is also well known that $ZnAl_2O_4$ and $ZnGa_2O_4$ are structurally isomorphous, where the Al^{3+} and Ga^{3+} cations are interchangeable, and a compound that contains both aluminum and gallium i.e., spinel phase, can be synthesized [9].

Hydrothermal synthesis has been known as a powerful method for the preparation of fine, high-purity and multicomponent oxide powders [10]. Several compounds with a spinel structure have been synthesized by solid-phase reaction at high temperature [11]. Besides their high-energy consumption, these solid-phase reactions require a series of laborious heating cycles at high temperatures and repeated grinding of starting oxide components. Regarding the preparation methods, spinels are easily obtained by co-precipitation of metal hydroxides followed by calcinations at temperatures between 750 and 1000 °C [12]. Moreover, a disadvantage of such materials for catalytic applications is the low surface area, usually about 20–50 $m^2\ g^{-1}$ [13]. Better

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results may be obtained by sol–gel methods. However, the disadvantages of the sol–gel process are the relative high costs of the metal alkoxides and the release of large amounts of alcohol during the calcinations step, which requires safety considerations.

Among many methods, hydrothermal synthesis, which can be defined as the treatment of aqueous solutions or precursors at elevated temperatures in pressurized vessels, is particularly promising for low-cost/low-temperatures production of advanced catalysts with required particle characteristics. Because crystalline powders are directly produced in the hydrothermal treatment, the need for high temperature calcinations and milling procedures to remove aggregates is eliminated, which may lead to form well-crystalline catalysts with high surface area. Few hydrothermal synthesis of zinc gallate ($ZnGa_2O_4$) and zinc aluminate ($ZnAl_2O_4$) spinels are known [14,15]. To the best of our knowledge, hydrothermal synthesis of $ZnO–Ga_2O_3–Al_2O_3$ spinel and its catalytic properties has not been investigated. In this study, we report a hydrothermal method for the preparation of spinel powders with a high surface area particularly useful for catalytic applications.

2. Experimental

2.1. Catalyst preparation

$Ga(NO)_3 \cdot 4 \cdot 7H_2O$ (High purity Chemical), $Al(NO_3)_3 \cdot 9H_2O$ (High purity Chemical), $Zn(NO_3)_2 \cdot 6H_2O$ (High purity Chemical) were used as raw materials. The content of ZnO, Al_2O_3 and Ga_2O_3 were 30, 40 and 30 mol%, respectively. Appropriate amounts of starting nitrates were dissolved in distilled water and aqueous ammonium carbonate ($(NH_4)_2CO_3$) solution (4.1 mol dm^{-3}) was added to the solution to co-precipitate metallic ions. In this procedure, the pH of the mixed solution was kept at ca. 8.5 and then the solution was vigorously stirred for 24 h. The precursor suspension was poured into a Teflon bottle with an inner volume of 25 cm^3 held in a stainless-steel vessel followed by flushing with N_2. After the vessel was sealed, hydrothermal reactions was performed at temperatures ranging from 110 to 250 °C for 14–48 h using a 500 ml-capacity autoclave with a magnetically driven stirrer (Model TPR-1, Taiatsu Techno). The resulting powders were repeatedly washed by centrifugation with deionized water three times, followed by drying at 110 °C. In this study $Ga_2O_3–Al_2O_3$ catalysts was synthesized by co-precipitation method. Ga-ZSM-5 ($SiO_2/Al_2O_3 = 23.3$, 115% in ion exchange ratio) was synthesized according to the method by Kikuchi *et al.* [16]. Co-ZSM-5 ($SiO_2/Al_2O_3 = 23.3$, 109% in ion exchange ratio) was synthesized from NH_4-ZSM-5 by ion exchange using an aqueous solution of metal acetate for 12 h at 80 °C. The ion exchange procedure was repeated three times.

2.2. Sample characterization

The crystalline phases were identified by X-ray diffractometry (XRD, Phillips APD 1700) using Cu$K\alpha$ radiation at 40 kV and 100 mA with a monochromator over a 2θ range from 10° to 70° at a scan rate of 2° min^{-1}. Particle size and surface area of the powders were determined by laser diffraction method (Nikkiso, Microtrac HRA 9320-X100/UPA 9340) and Brunauer–Emmett–Teller (BET) nitrogen adsorption technique at 77 K with a conventional flow type apparatus (Coulter, Omnisorp 360), respectively. Surface acidity, i.e., the concentration of Lewis and Brønsted centers on the sample surface, was established by means of IR spectroscopy in accordance with a procedure described in the literature [17], using pyridine as the probe molecule. The IR spectra were recorded at room temperature with a Specord M80 spectrometer.

2.3. Catalytic activity measurement

The catalytic activity of the resulting powder was measured using a fixed bed flow reactor. The sample powders of 180 mg were placed between quartz wool plugs in the reactor and then pretreated in a helium flow at 400 °C for 2 h in order to eliminate possible contaminants such as adsorbed water. The gas flow rate was fixed at 60 cm^3 min^{-1}. The effluent gas was analyzed with intervals of 15 min by an online gas chromatograph (GC, Chrompack CP-2002) with columns of Porapak Q (CO_2, N_2O) and Molecular Sieve 5A (O_2, N_2, NO, CO). NO conversion and total NO_x in the reactor effluent was detected using a chemiluminescent NO–NO_x gas analyzer (BEST Instrument, BSU-100uH). The catalytic activity was evaluated in terms of NO to N_2 and that of the reducing agent to COx (CO + CO_2). The formation of N_2O was negligible. NO conversion to N_2 and hydrocarbons conversion to CO_2 calculations are based on the following expressions:

$$\text{NO conversion to } N_2(\%) = \{2[N_2]/[NO]^{in}\} \times 100$$
$$CH_4 \text{ conversion to } CO_2(\%) = \{(1)[CO_2]/[CH_4]^{in}\} \times 100$$
$$C_2H_4 \text{ conversion to } CO_2(\%) = \{(1/2)[CO_2]/[C_2H_4]^{in}\} \times 100$$
$$C_3H_6 \text{ conversion to } CO_2(\%) = \{(1/3)[CO_2]/[C_3H_6]^{in}\} \times 100$$

where $[NO]^{in}$, $[CH_4]^{in}$, $[C_2H_4]^{in}$ or $[C_3H_6]^{in}$ are the inlet NO, CH_4, C_2H_4 or C_3H_6 concentration, respectively and $[N_2]$ or $[CO_2]$ are the concentration of N_2, or CO_2 in the reactor effluent gas.

3. Results and discussion

3.1. Characterization of catalysts

The effect of treatment temperature on the solid products formed by hydrothermal treatment at 100–250 °C for 14–48 h from mixed solution of 30 mol% ZnO, 40 mol% Al_2O_3 and 30 mol% Ga_2O_3 is shown in figure 1. In the specimens treated at 110 °C, the main solid product was GaO(OH), together with a spinel phase detected as a broad peak at around $2\theta = 36.2°$. In the reaction conditions 150 °C for 14 h (figure 1(c)), only spinel phase was detected from the XRD results. Graphs for the XRD spectra did not show any excess ZnO, A_2O_3, or Ga_2O_3 that were present as unreacted material as shown in figure 1(c). Figure 2(b) shows the XRD patterns of $ZnO–Ga_2O_3–Al_2O_3$ after the de-NO_x test, no additional peaks were detected after the catalytic test. A small increase in the peak intensity was observed in the XRD pattern of $ZnO–Ga_2O_3–Al_2O_3$, indicating an increased crystalinity of $ZnO–Ga_2O_3–Al_2O_3$. After the thermal treatment at higher temperatures, an increase in the degree of crystallinity and in the crystallite size was readily noticeable as shown in figure 2(c).

3.2. Catalytic performance

Low temperature and direct synthesis of crystalline ceramic particles is of current interest and may meet the requirements not only from performance of ceramics, including spinel, but also from global problems related with energy, resources and environment. In this study, fine particles of crystalline spinel powders were successfully obtained by direct precipitation from aqueous solution below 150 °C under hydrothermal process. The BET surface area of the $ZnO–Ga_2O_3–Al_2O_3$ catalyst was found to be 150 $m^2\ g^{-1}$ prepared by hydrothermal method.

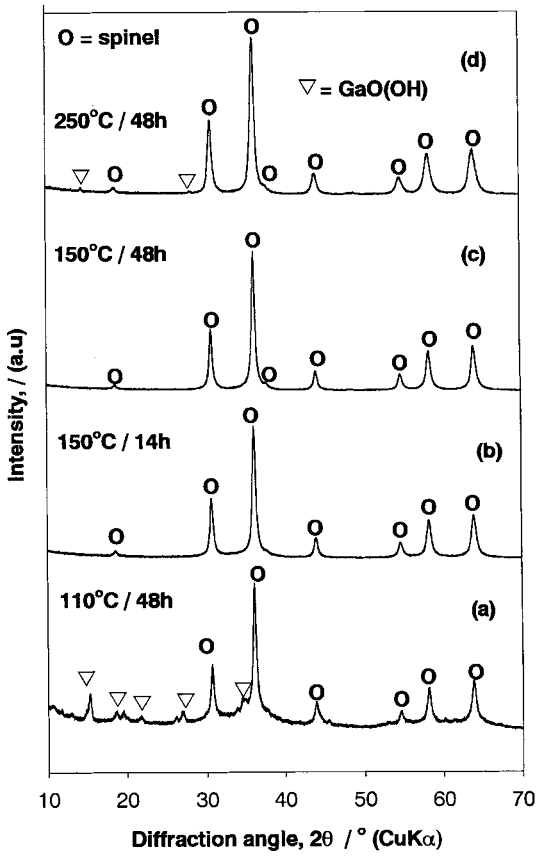

Figure 1. X-ray diffraction patterns of $ZnO–Ga_2O_3–Al_2O_3$ spinel phase synthesized by hydrothermal treatment at 110 to 250 °C for 48 h.

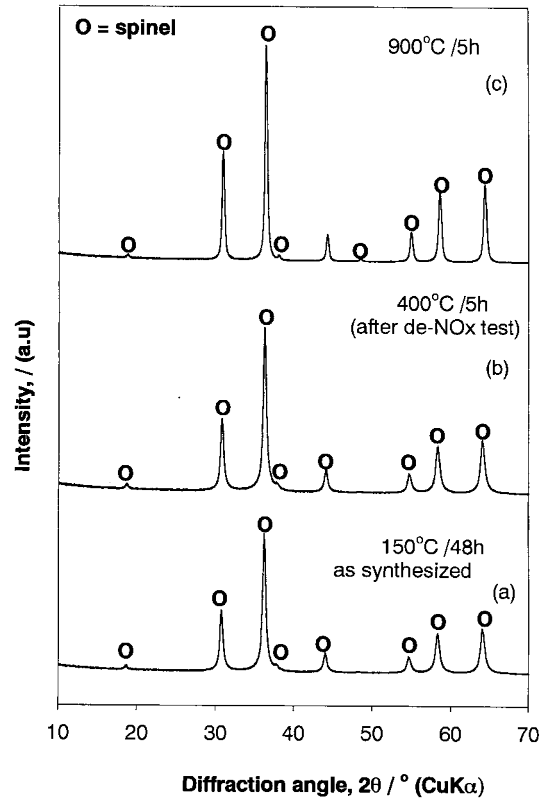

Figure 2. X-ray diffraction patterns of calcined $ZnO–Ga_2O_3–Al_2O_3$ and after de-NO_x test, synthesized by hydrothermal treatment at 150 °C for 48 h.

Figure 3 shows the activity of $ZnO–Ga_2O_3–Al_2O_3$ catalyst for NO reduction by C_2H_4 in the presence of oxygen. Although $Ga_2O_3–Al_2O_3$ catalyzed effectively the NO reduction by C_2H_4 with high NO conversion of more than 98% in the temperature range of 450–500 °C, ZnO enhanced further the activity of $Ga_2O_3–Al_2O_3$ over a wider range of temperature 400–600 °C. The temperature range of the catalytic activity for the $Ga_2O_3–Al_2O_3$ powder was similar to that previously reported [1]. From figure 3, we can see that the conversion of NO on $ZnO–Ga_2O_3–Al_2O_3$ is much higher in a wider temperature range than that on the $Ga_2O_3–Al_2O_3$. As the temperature was increased to above 500 °C, the conversion of NO on the $Ga_2O_3–Al_2O_3$ began to decline very sharply, while that on the $ZnO–Ga_2O_3–Al_2O_3$ continued to maintain high reduction activity at 600 °C. It seems that the incorporation of Zn^{2+} ions into Ga sites in the spinel structure improved the NO reduction activities. This is because the substituted ZnO in the $Ga_2O_3–Al_2O_3$ framework with elecrophilic d-orbital tends to produced a cooperative effect together with Ga^{3+} because Ga^{3+} ions have strong preference for

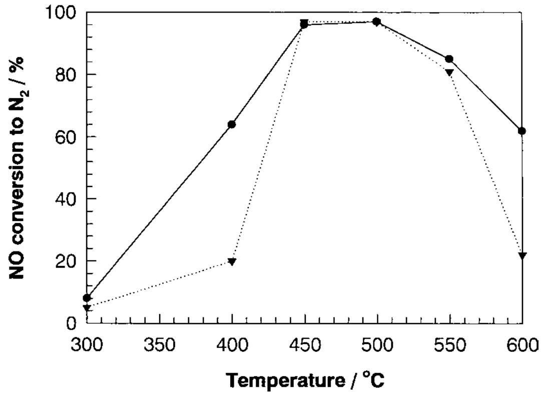

Figure 3. Selective reduction of NO by C_2H_4 on ZnO–Ga_2O_3–Al_2O_3 (●) and on Ga_2O_3–Al_2O_3 (▼) as a function of reaction temperature. The reaction was run with a feed consisting of 1000 ppm NO, 1000 ppm C_2H_4, 10% O_2 balanced by He at a flow rate 60 cm^3 min^{-1} and catalyst weight 0.18 g.

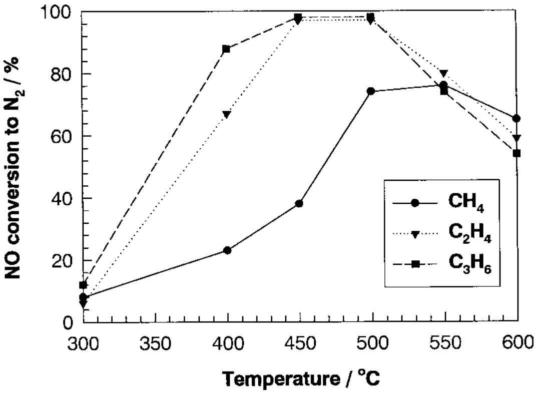

Figure 4. Selective reduction of NO by 1000 ppm CH_4 (●), 1000 ppm C_2H_4 (▼) and 1000 ppm C_3H_6 (■) on Zn–Ga_2O_3–Al_2O_3 as a function of reaction temperature. The reaction was run with a feed consisting of 1000 ppm NO, 10% O_2 balanced by He at a flow rate 60 cm^3 min^{-1} and catalyst weight 0.18 g.

tetrahedral sites [18] and it might be assumed that ZnO should go to the same tetrahedral position therefore the cooperative effect from ZnO and Ga_2O_3 could accelerate the NO activation preferentially, resulting in the improvement of NO reduction.

The maximum NO conversion on ZnO–Ga_2O_3–Al_2O_3 was identical when compared with Ga_2O_3–Al_2O_3. On the other hand, in the case of In_2O_3-, SnO_2-, CoO-, CuO- and Ag-doped Ga_2O_3–Al_2O_3, the maximum NO conversion was much less than that on Ga_2O_3–Al_2O_3 [7]. This is because hydrocarbon oxidation by oxygen, which is a side reaction-consuming hydrocarbon, proceeds predominantly because of the too high oxidation activity of CuO and Ag. In the case of In_2O_3 and SnO_2, NO reduction also decreased, although their propene oxidation activity was not so high.

The activity of FeO–Ga_2O_3–Al_2O_3 was also low and it can be assumed that the presence of large iron oxide particles catalyzing C_2H_4 oxidation with dioxygen.

3.3. NO reduction by hydrocarbons

Reductants such as propane, propene and ethylene have been extensively researched on zeolite- and alumina-supported catalysts [19]. Use of CH_4 as a reducing agent, pioneered by the work of Li and Armor [20], has attracted particular interest, since CH_4 is present in almost all combustion exhausts, particularly in the gas-cogeneration system. Figure 4 shows that ZnO–Ga_2O_3–Al_2O_3 catalysts are active not only by C_2H_4, C_3H_6 but also by CH_4 in the presence of oxygen. Figure 4 also shows the NO conversion with C_3H_6 was slightly shifted at lower temperature region than that with C_2H_4. In an effort to explain these kinds of results, some authors have proposed a so-called kinetics antagonism phenomenon probably caused, as suggested, by the preferential adsorption and diffusion of C_2H_4 within the catalyst micropore structure as compared to C_3H_6. Moreover, it should be noted that as the carbon number increased, the temperature range at which NO reduction occurs shifted to the lower temperature region [19].

It has been reported that hydrocarbon activation proceeds on acid sites by the formation of hydrocarbon-derived adspecies [1]. It might be assumed that the addition of ZnO into Ga_2O_3–Al_2O_3 with spinel phase causes an increase of the number of acid sites. The presence of strong acid sites in the sample was established by means of IR spectroscopy as shown in figure 5. It has been found that considerable information can be obtained about the acidity of various solids by studying changes in the "ring" vibrations of pyridine and other bands in the region of 1700–1400 cm^{-1} [21]. The bands in the 1440–1455 cm^{-1} region can be used to indicate Lewis acidity. The retention of pyridine after evacuation at high temperatures, as evidenced by the frequency shift of the 1583 cm^{-1} band to 1599 cm^{-1}, is indicative that the dehydrated spinel catalyst is a strong Lewis acid.

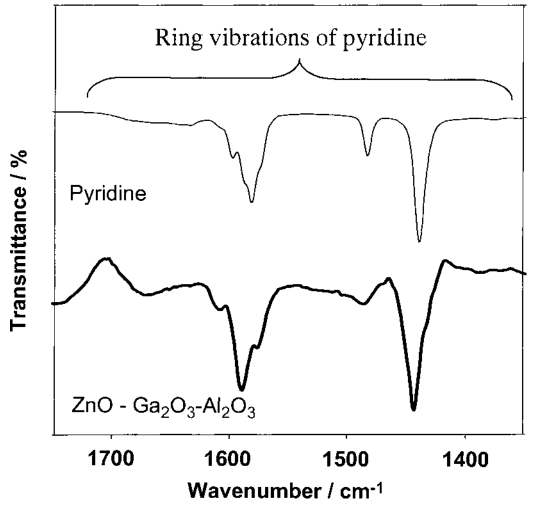

Figure 5. Infrared spectra of pyridine adsorbed on ZnO–Ga_2O_3–Al_2O_3.

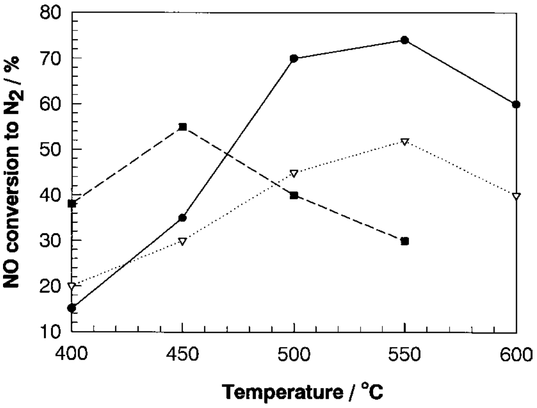

Figure 6. Selective reduction of NO by CH_4 on $ZnO–Ga_2O_3–Al_2O_3$ (●), on Ga-ZSM-5 (■), and on Co-ZSM-5 (▽) as a function of reaction temperature. The reaction was run with a feed consisting of 1000 ppm NO, 1000 ppm CH_4, 10% O_2 balanced by He at a flow rate 60 cm^3 min^{-1} and catalyst weight 0.18 g.

3.4. Comparison with ZSM-5 catalysts

Figure 6 compares the activity of $ZnO–Ga_2O_3–Al_2O_3$ with ZSM-5 based catalysts which have been reported to be effective for SCR of NO by CH_4 [16,22]. At low temperature, the NO conversion decreased in a sequence of Co-ZSM-5 > Ga-ZSM-5 > $ZnO–Ga_2O_3–Al_2O_3$. At high temperature, on the other hand, NO conversion was highest on $ZnO–Ga_2O_3–Al_2O_3$, and Ga-ZSM-5 followed it. A bend over of the NO conversion profile was drastic on Co-ZSM-5, resulting in the quite lower conversion of NO at high temperature.

Figure 7 shows NO conversion when 2.5% water vapor was added to the reactant feed. From the comparison with figure 6, it is shown that NO conversion decreased by water vapor on all the catalysts. As reported [16,22], Ga-ZSM-5 was more sensitive to water vapor than Co-ZSM-5. In contrast, $ZnO–Ga_2O_3–Al_2O_3$ moderately reduced NO even in the presence of water vapor especially at high temperatures. The NO conversion was the highest on $ZnO–Ga_2O_3–Al_2O_3$ at high temperatures.

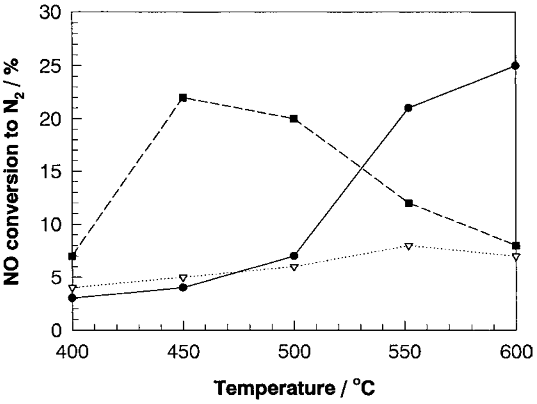

Figure 7. Selective reduction of NO by CH_4 in the presence of 2.5% water vapor on $ZnO–Ga_2O_3–Al_2O_3$ (●), on Ga-ZSM-5 (▽), and on Co-ZSM-5 (■). The reaction was run with a feed consisting of 1000 ppm NO, 1000 ppm CH_4, 10% O_2 balanced by He at a flow rate 60 cm^3 min^{-1} and catalyst weight 0.18 g.

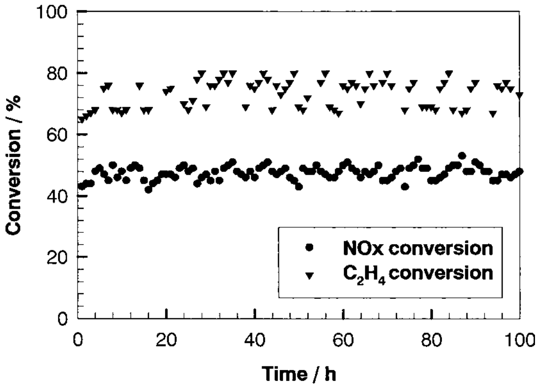

Figure 8. Durability in the presence of water vapor and sulfur dioxide of $Zn–Ga_2O_3–Al_2O_3$ at 500 °C. The reaction was run with a feed consisting of 500 ppm NO, 500 ppm C_2H_4, 10% O_2, 10% water vapor, 3 ppm SO_2 balanced by He at a flow rate 250 cm^3 min^{-1} and catalyst weight 0.5 g.

3.5. Lifetime

The catalyst was formed into pellets, crushed, and sieved into 1–2 mm grains before the catalytic durability tests in presence of water vapor. The reaction was run with a feed consisting of 500 ppm NO, 500 ppm C_2H_4, 10% O_2 and 10% water vapor balanced by He at a flow rate 250 cm^3 min^{-1}. $ZnO–Ga_2O_3–Al_2O_3$ spinel was found to have high durability at 500 °C for the reduction of NO by C_2H_4 in the presence 10% water vapor and stable NO conversions was obtained over 100 h. We also examined the effect of SO_2 over $ZnO–Ga_2O_3–Al_2O_3$ catalyst in the presence of water vapor and no deactivation was found in presence of 3 ppm SO_2 as shown in figure 8.

4. Conclusions

$ZnO–Ga_2O_3–Al_2O_3$ spinel powders with interesting properties from a catalytic point of view were successfully synthesized by hydrothermal method. The proposed synthesis, in contrast to other methods, does not require high temperature calcinations to obtain the spinel phase. The catalytic data presented in this work, as a whole, clearly indicate that ZnO containing $Ga_2O_3–Al_2O_3$ is an effective catalyst for the reduction of NO by CH_4, C_2H_4 and C_3H_6. No deactivation behavior was observed for the reduction of NO by C_2H_4 during continuous reaction conditions in the presence of water vapor and SO_2 at 500 °C.

Acknowledgments

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