Multi-Component Catalysts with Spinel Structure for the Selective Reduction of Nitrogen Oxide by Ethylene in Lean-Exhaust Gas Streams[1]

Md. Hasan Zahir[a], Alhooshani K[a], Mohammad A. Jafar Mazumder[a], and Toshio Suzuki[b]

[a] *Chemistry Department, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia*
[b] *Advanced manufacturing Research Institute, National Institute of Advanced Industrial Science and Technology, Nagoya, Japan*
e-mail: hzahir@kfupm.edu.sa
Received July 26, 2012

Abstract—The Ga_2O_3–Al_2O_3–ZnO (GAZ) multi–component spinel powders with incorporated Cu^{2+}, Co^{2+}, Fe^{2+}, Ni^{2+}, Mn^{2+} and In^{2+} metal cations were synthesized by co–precipitation method from a mixed solution of nitrate salts. Spinel crystal structure of each composition was confirmed by XRD measurements. The multi–component oxide powders were tested in the reduction of nitrogen oxide (NO) under lean conditions. Among the catalysts tested, In_2O_3–containing GAZ with a pure spinel phase structure showed promising catalytic activity in the NO reduction in the presence of 10% H_2O vapor. In addition, the effect of H_2O vapor and SO_2 on the selective reduction of NO over In_2O_3–GAZ/cordierite and In_2O_3–GAZ/metal honeycombs catalysts has been investigated.

Nitrogen oxides ($NO_x = NO + NO_2$) emitted from the gasoline and diesel exhaust represent one of the major environmental problems. Selective catalytic reduction (SCR) of NO_x by hydrocarbons (HC) is an effective way to remove NO from the exhaust gases. Over the last decade, there have been considerable efforts to investigate the performance of various catalysts in HC–SCR [1, 2]. It is well known that the systems based on three–way catalysts and zeolite catalysts are unstable in real exhaust conditions particularly in the presence of O_2 and H_2O vapor. Therefore, various attempts have been made to develop more suitable catalysts. Among all studied catalysts, metal oxide based catalysts were found promising due to their high thermal stability. Hamada et al. [3] used Ga_2O_3–Al_2O_3 (GA) and/or GA systems doped with Ni^{2+}, Ag^{2+}, Co^{2+}, Cu^{2+}, In^{2+} and Sn^{2+} on γ-Al_2O_3 for NO_x reduction. They found that Ga_2O_3 and In_2O_3 oxides carried by acidic supports, such as γ-Al_2O_3, TiO_2, and SiO_2–Al_2O_3, showed high de–NO_x activity [4]. The authors also demonstrated the effect of double dopants (Ga_2O_3 and ZnO) into Al_2O_3 (i.e., Ga_2O_3–Al_2O_3–ZnO (GAZ) system)) with spinel structure, and found good catalytic activity and selectivity similar to Ga–ZSM–5 for SCR of NO [5, 6]. The GAZ system with spinal structure showed exceptionally high NO reduction activity even after calcinations at 1000°C [7]. However, decreasing NO reduction activity in the presence of H_2O limits the applicability of GAZ system.

Among the γ-Al_2O_3–supported materials, In–Al_2O_3 and In–GA nanocomposites revealed the highest performance in terms of the N_2 yield and hydrocarbon selectivity [8]. Catalysts based on In_2O_3 supported by γ-Al_2O_3 have been thoroughly investigated over the years [4, 8]. However, no studies have been reported on In_2O_3 containing Al_2O_3 with spinel type catalysts. In general, γ-Al_2O_3 show a phase transition to α-Al_2O_3 around 800°C and once the phase transition occurrs the catalytic activity of γ-Al_2O_3 based catalysts decreases significantly. Although the phase transition temperature of γ-Al_2O_3 is higher than the temperature of exhaust gases, the thermal stability of the γ-Al_2O_3 based catalyst is unreliable because of the possibility of local increases n temperature in practical use. Therefore, the In_2O_3 containing Al_2O_3 with spinel structure might be a promising NO reduction system particularly in the presence of H_2O vapor at high temperature. Generally, most of the investigations focus on single–component catalysts. So far no attempts have been made to study multi–component catalyst formulations consisting of several active elements on the alumina support. Mixed metal oxides catalysts, containing more than one kind of metal atom are widely used in several fields of research related to catalysis [9, 10]. The addition of multivalent and/or multi–component transition metal ions may adversely affect selectivity because these ions are active in the catalytic oxidation of hydrocarbons [9]. However, NO reduction activity over multi-component metal oxides system is scant and it is desirable to find a way to enhance the activity [9].

---

[1] The article is published in the original.

Most of the NO_x catalysts have been prepared in the form of powders or pellets, which could not meet requirements of practical applications. The catalytic performance over honeycomb system washcoated with the In—GAZ, which plays an important factor in the development of automotive catalysts, has not been explored yet. Typically, both metal and ceramic monoliths are employed for automotive catalysts nowadays. The popular design for the automotive exhaust catalysts is the monolith catalysts. A monolith has a honeycomb structure with parallel and usually straight channels or cells, and the catalyst particles are dispersed on the wall of the channels. Compared with packed-bed reactors loaded with pellet catalysts, the monolith has several advantages such as low pressure—drop (up to two orders of magnitude) [11], high—geometric surface, robustness, low weight and better heat transfer rate [12]. Traditionally, cordierite monoliths have been used quite extensively, due to their lower production cost. Metal monoliths have other merits such as high mechanical strength, high thermal conductivity, and durability [13].

In this study, the effect of Ni^{2+}, Co^{2+}, Cu^{2+}, Fe^{2+}, Mn^{2+} and In^{2+} metal oxide on Ga_2O_3—Al_2O_3—ZnO with spinel structure has been investigated inr the selective reduction of NO with C_2H_4. These studies were aimed at improving the activity of GAZ system in the presence of H_2O vapor and SO_2. NO reduction activity over cordierite and metal honeycombs systems washcoated with the In_2O_3—GAZ multi—component spinel catalyst system has also been investigated in order to verify, whether the catalysts were good candidate for practical lean NO catalysts.

EXPERIMENTAL
Materials and Synthesis

The loading of Ga_2O_3 was fixed at 30 mol%, while that of ZnO was 30 mol % in the case of Ga_2O_3—Al_2O_3—ZnO system. In^{2+}, Co^{2+}, Cu^{2+}, Fe^{2+}, Mn^{2+} and Ni^{2+} were selected as the metal oxide additive. The composition of starting nitrates was M : Ga : Al : Zn = 5 : 30 : 35 : 30 mol%, and it is known that the catalyst containing 30 mol% of Ga_2O_3 gives the highest catalytic activity in the de—NO_x reactions in the Ga_2O_3—Al_2O_3 (GA) system [5]. Appropriate amounts of starting nitrates were dissolved in distilled water and aqueous ammonium carbonate solution was added to the solution to co—precipitate metallic ions. The pH of the solution was maintained at ca. 8.5 and the solution was vigorously stirred for 24 h. The obtained precipitate was washed thoroughly with distilled water, followed by drying at 110°C and heat treatment at 800°C for 5 h in air.

Preparation of Honeycombs Washcoated with In₂O₃—GAZ Spinel

The washcoating slurry was prepared by mixing the In_2O_3—GAZ, alumina sol and distilled water in the weight ratio of 14.3 : 8.4 : 77.3. At present, synthetic or

Physical properties of washcoated cordierite honeycombs employed in the present study

---

Cell type circular parallel channels (cordierite), zigzag square channel, metal

Cell density: 900 cpsi, for cordierite and metal honeycombs

Washcoated catalyst: In doped—GAZ spinel

Average thickness of washcoat: 18μm, Cordierite

* Washcoats = GAZ + alumina binder;
** Cpsi = number of cellsin^{-2}.

natural alumosilicate—cordierite, with a low specific surface area, not exceeding 0.2–$0.4 \ m^2 g^{-1}$, is most frequently applied to form a honeycomb structure. In this study, alumina sol (Alumina sol 520, Nissan Chemical Industries, Ltd.) was used, which acted as an inorganic binder. The commercial cordierite and metal honeycombs were immersed in the slurry and then withdrawn, followed by drying. The excess suspension inside the channels of the cordierite substrate was blown off. Before the introduction of wash coat of Al_2O_3, the metal honeycomb was pretreated by thermal oxidation at 800°C for 5 he in static air atmosphere. Since the suspension cannot be coated sufficiently by a single impregnation, multi—impregnation was required. The coated honeycombs were heat treated at 800°C for 5 h. The physical properties of the washcoated honeycombs employed in the present study are listed in table.

Catalytic Activity Measurements

The catalytic activity of the resulting powder and honeycomb washcoated with GAZ spinel was measured using a fixed bed flow pyrex glass tubular reactor with an internal diameter of 10 mm for powder and 32 mm for monolith catalysts. For both cases, the samples were placed between quartz wool plugs in the reactor.

A commercial cordierite honeycomb composed of MgO—Al_2O_3—SiO_2 and a metal monolith composed of Fe—Cr—Al, were also tested. Honeycombs (cordierite and metal) of the same size (50 mm in length, 25 mm in width, and 40 mm in height) were used as the substrate. The reactor space velocity was defined as the ratio of the total volumetric flow rate to the volume of the monolith reactor. However, in the case of powders samples, the space velocity was defined as the total flow rate related to the weight of catalysts. Dead space between the honeycomb catalyst and the reactor wall was filled with an inert material to prevent breakthrough of gas. All the lines were heated to avoid possible water condensation.

The flow rate of each gaseous reactant was regulated by a mass—flow controller (STEC Inc.). The flow of each gas was fixed and held constant with a 4—channel electronic mass-flow controller (UCAR Instruments,
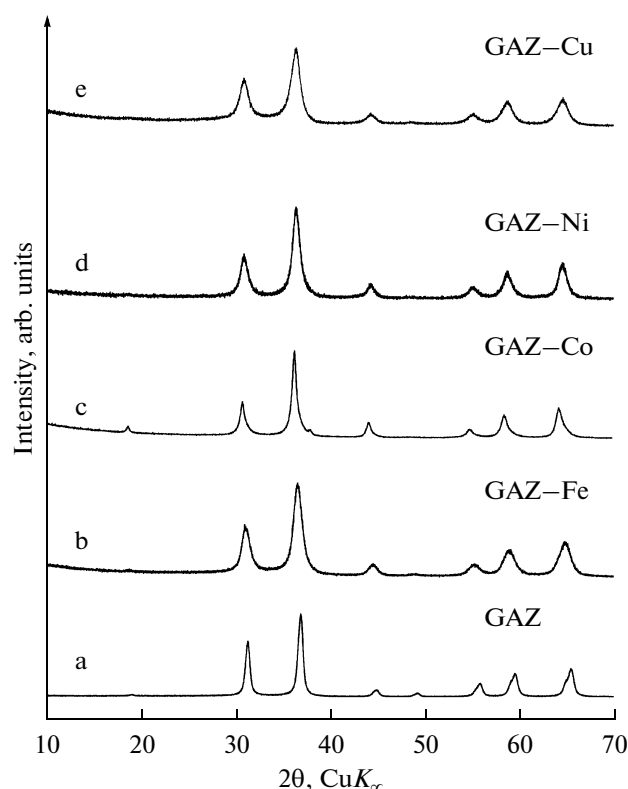
Fig. 1. X—ray diffraction patterns of GAZ(a), Fe—GAZ(b), Co—GAZ(c), Ni—GAZ(d) and Cu—GAZ(e). The composition of GAZ was Ga : Al : Zn = 30 : 40 : 30 and M—GAZ was M : Ga : Al : Zn = 5 : 30 : 35 : 30 mol% (M = Fe, Co, Ni and Cu). All samples were heat-treated in air at 800°C for 5 h.

MFB—21—1). A temperature controller (Leeds & Northrup Instruments, Electromax V Plus) was used both to increase the furnace temperature at a linear heating rate of 10 K min⁻¹ and to hold the temperature constant at any selected value. The catalysts were activated prior to measurements by increasing the temperature from 300 to 600°C under reaction feed and holding the samples at 600°C for 30 min. Measurements were then taken downwards from 600 to 300°C with a step of 50°C after 30 min stabilization at each reaction temperature. In some experiments, H_2O and SO_2 were introduced into the reaction gas mixture at a concentration of 10% and 3 ppm, respectively. H_2O vapor was introduced into the reaction gas mixture with a micro pump. In this case, the catalyst had been pre—treated at 600°C for 12 h in a flowing gas containing 1000 ppm NO, 10% O_2, 3 ppm SO_2 and 10% H_2O diluted in He, in order to stabilize the catalytic activity. 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 calculated using a chemiluminescent NO—NO_x gas analyzer (BEST Instrument, BSU—100 uH). Calibration was done with

a standard gas containing known concentrations of the components.

Blank experiment carried out by passing the reactant streams through the empty reactor showed that no NO_x conversion occurred without catalyst. Moreover, at the beginning of each experiment, the catalyst was purged with the reaction gas until the NO concentration of the exit gas reached the inlet gas concentration.

Nitrogen formation was used to calculate the NO conversion and the hydrocarbon consumption was used to calculate the hydrocarbon conversion. The catalytic activity was evaluated in terms of conversion of NO to N_2 and conversion of the reducing agent to CO_x(CO + CO_2). The mass balance of N_2 was reasonable within an error of 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:

$$NO \text{ conversion to } N_2 (\%) = \{2[N_2]/[NO]^{in}\} \times 100$$

$$C_2H_4 \text{ conversion to } CO_2 (\%)$$
$$= \{(1/2)[CO_2]/[C_2H_4]^{in}\} \times 100.$$

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

Characterization

XRD patterns were recorded using an X—ray diffractometer (XRD, Phillips APD 1700) with a CuK_α radiation source of 40 keV and 40 mA equipped a monochromator; measurements were taken in the ≤10 2θ ≥ 70° range at a scan rate of 2° min⁻¹. Particle size and surface area of the powders were determined by a laser diffraction method (Nikkiso, Microtrac HRA 9320—X100/UPA 9340) and by the Brunauer—Emmett—Teller (B.E.T.) nitrogen adsorption technique, respectively.

RESULTS AND DISCUSSION
Addition of Cu^{2+}, Ni^{2+}, Co^{2+} and Fe^{2+} into GAZ

Figure 1 shows the XRD patterns of GAZ recorded upon addition of Cu^{2+}, Ni^{2+}, Co^{2+} and Fe^{2+} cations. As—prepared powders of the GAZ samples doped with metal oxides were non—crystalline, whereas the samples calcined at 800°C showed peaks of crystalline phases. Fe^{2+} containing GA showed diffraction peaks for both γ-Al_2O_3 and Fe oxides [6]. The GAZ sample containing Fe^{2+} shows only diffraction peaks corresponding to a spinel phase. Samples with Co^{2+}, Ni^{2+} and Cu^{2+} ions showed XRD diffraction peaks that correspond to a spinel phase (Fig. 1).

GAZ powders containing Cu^{2+}, Ni^{2+}, Co^{2+} and Fe^{2+} were examined in the NO reduction by C_2H_4 as a function of temperature in the presence (Fig. 2b) and absence of H_2O vapor (Fig. 2a). In the absence of metal cations, GAZ showed the maximum NO conversion at temperatures from 400 to 500°C (Fig. 2a). GAZ powders with Cu^{2+} cations showed low NO conversion
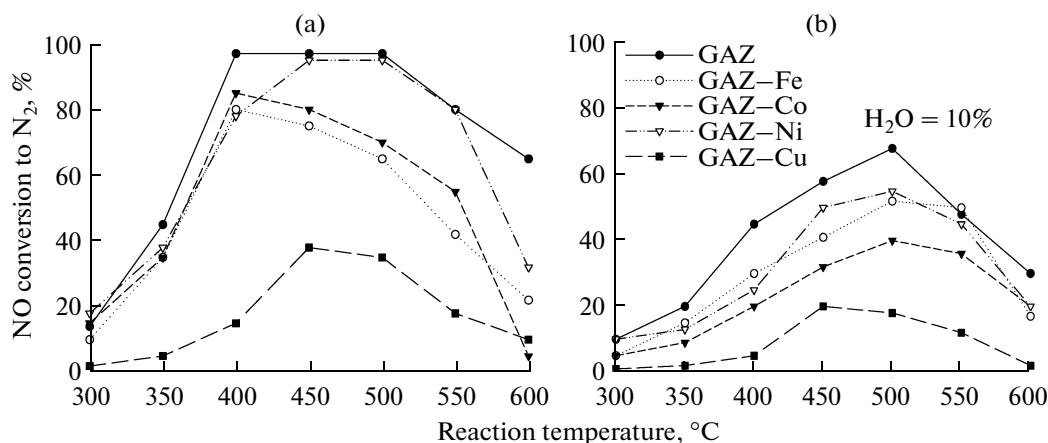
Fig. 2. Catalytic activity of the GAZ and M−GAZ (M = Fe, Co, Ni and Cu) in the NO reduction as a function of reaction temperature in the absence (a) and in the presence of 10% H_2O vapor. Feed composition: NO = 1000 ppm, C_2H_4 = 2000 ppm, O_2 = 10% and balanced by He; catalyst weight = 0.18 g; GHSV: 20000 h^{-1}.

(<40%) at temperatures ranging from 400 to 600°C (Fig. 2a). However, the GAZ catalyst with Ni^{2+} showed higher NO conversion than GAZ samples doped with Cu^{2+}, Co^{2+} and Fe^{2+} and maximum NO conversion was observed over the range from 450 to 500°C. The low catalytic activities of the GAZ samples doped with Co^{2+} and Cu^{2+} cations might be due to the hydrocarbon oxidation by oxygen, which is a side reaction that consumes the hydrocarbon. The reaction proceeds predominantly because Co^{2+} and Cu^{2+} ions are highly active in the oxidation [14]. It was observed that the activity of GAZ was suppressed in the presence of H_2O vapor (Fig. 2b), and the maximum of activity was shifted to higher temperatures. A similar retarding effect of H_2O vapor was observed for Co^{2+}, Cu^{2+}, Fe^{2+}, and Ni^{2+}−containing GAZ system. In the presence of H_2O vapor, however, the GAZ catalyst and the GAZ sample doped with Ni^{2+} showed higher reduction activity than other tested GAZ systems doped with cations (Co^{2+}, Cu^{2+}, Fe^{2+}) (Fig. 2b).

The surface area of Ni^{2+}−doped GAZ powders was 70 $m^2 g^{-1}$ whereas GAZ powders showed a smaller surface area of 48 $m^2 g^{-1}$. Despite the lower surface area, GAZ powders exhibited a high catalytic activity similar to GA. It appears that the simultaneous addition of Ni^{2+} and Zn^{2+} to the GAZ might enhance the catalytic activity. It was therefore of interest to examine the changes in the NO reduction activity caused by the addition of double dopants Ni^{2+} and Zn^{2+} into the GAZ. The performance of the GAZ catalysts containing double dopants Ni^{2+} and Zn^{2+} was like that of typical zeolite based catalysts, and NO reduction activity was found to be somewhat higher over the temperature range of 300−500°C (Fig. 3). However, in the presence of H_2O vapor, the catalytic activity of Ni^{2+} and Zn^{2+} containing GAZ decreased (ca. 30%) with time.

### Addition of In^{2+} and Mn^{2+} Cations into GAZ

Transition metal oxide−based catalysts are less expensive than noble metal catalysts, which are in general more resistant to H_2O vapor and SO_2 poisoning. Manganese oxides usually show good SCR activity at low temperatures [15]. Smirniotis et al [16] reported that pure MnO_x loaded on $TiO_2/Al_2O_3/SiO_2/AC$ (activated carbon) showed good SCR activity GAZ. It has also been reported that after the introduction of In^{2+} cation Al_2O_3 showed high activity in the NO reduction in the presence of H_2O and SO_2 [17, 18]. To date, In^{2+} doped Al_2O_3 with γ-Al_2O_3 structure has been studied by several research groups [8]. However, no report has been published in which In^{2+} doped was used in GAZ spinel structure. As mentioned earlier, the γ-Al_2O_3 phase is not stable and/or catalytic activity decreased signifi-
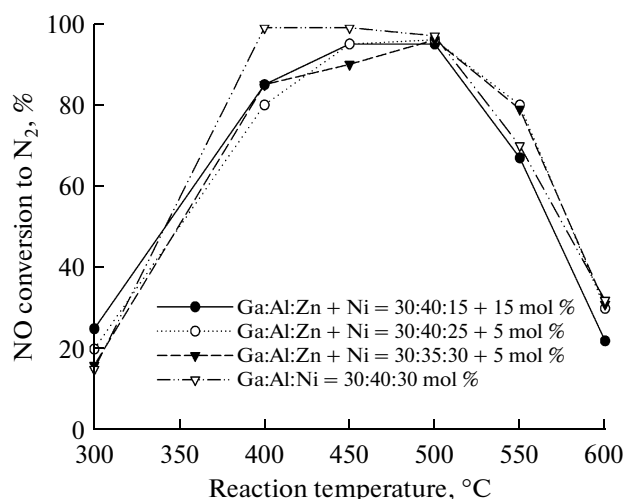
Fig. 3. The catalytic activity of Ga_2O_3−Al_2O_3 simultaneously doped with Zn and Ni oxides in the NO reduction as a function of the reaction temperature. The reaction conditions are the same as in Fig. 2a, GHSV−20000 h^{-1}.
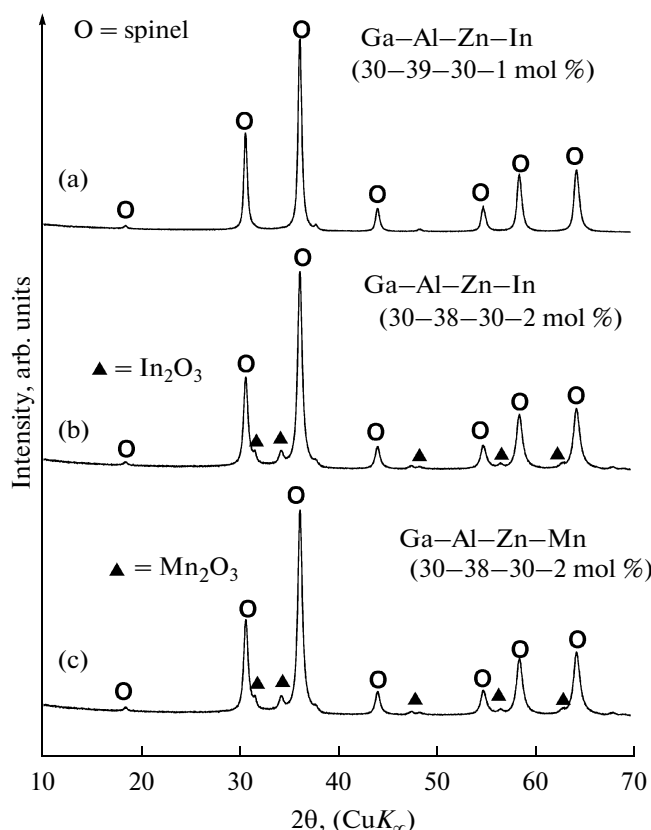
Fig. 4. X–ray diffraction patterns of GAZ doped with 1 mol% In (a), 2 mol% In (b) 2 mol% Mn (c). All samples were heat–treated in air at 800°C for 5 h.
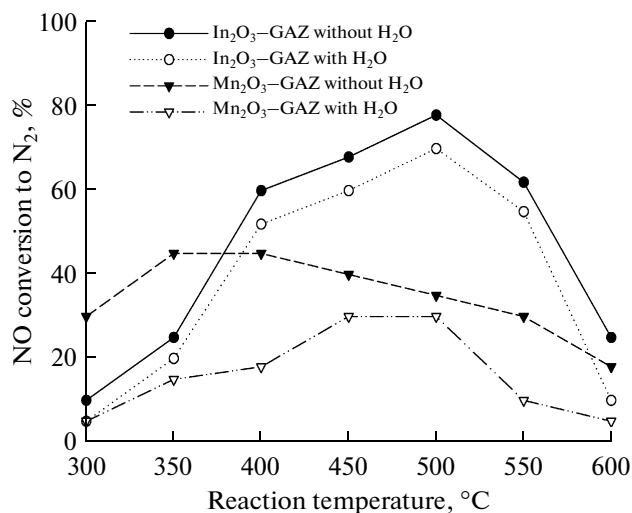
Fig. 5. The catalytic activity of 1 mol% In_2O_3–GAZ and 2 mol% Mn–GAZ in the NO reduction as a function of the reaction temperature. The reaction conditions are the same as in Fig. 2, GHSV: 20000 h^{-1}. Shaded symbols ● and ▼ denote the data obtained in the absence of H_2O vapor and the same open symbols signify the data obtained in the presence of 10% H_2O vapor.

cantly at higher temperature. Therefore, the addition of In^{2+} and Mn^{2+} cations into the GAZ spinel system was examined in a hope to prepare promising deNO$_x$ materials that would be active in the presence of H_2O vapor and SO_2.

Figure 4a shows that the additions of 1 mol% In^{2+} cation into the GAZ results in a single spinel phase with the composition of Ga–Al–Zn–In = 30 : 39 : 30 : 1. However, the GAZ sample with 2 mol% In^{2+} (Ga–Al–Zn–In = 30 : 38 : 30 : 2) appears to contain both spinel phase and a phase of$^+$ In_2O_3 (Fig. 4b). In the case of Mn^{2+} cation, the XRD pattern showed not only diffraction peaks corresponding to a spinel phase but also diffraction peaks associated with Mn oxides (Fig. 4 (c)). The NO reduction activity of In_2O_3–GAZ and Mn_2O_3–GAZ catalysts was studied (Fig. 5) as a function of temperature in the presence and absence of H_2O vapor using the reaction conditions indicated in Fig 2. Figure 5 shows that the overall NO conversion rate of In_2O_3–GAZ decreased slightly in the presence of H_2O vapor. Among the catalysts tested, In_2O_3–GAZ with a pure spinel phase structure exhibited the highest catalytic activity for NO reduction in the presence of H_2O vapor. In order to get information on the optimum loading of In_2O_3, the effect of In_2O_3 loading on the activity of In^{2+}–GAZ for NO reduction by C_2H_4 was also examined. When 2 mol% In_2O_3 was doped into the GAZ in the presence of H_2O vapor, the NO reduction at 450°C decreased from 60% to 40%. It was observed that the addition of 2 mol% In_2O_3 into the GAZ produces spinel and In_2O_3 phases. Therefore, it could be assumed that small amounts of In_2O_3 inhibit the oxidation of hydrocarbon, which subsequently reduces the rate of NO reduction. The plot of the NO conversion versus temperature for the In_2O_3–GAZ system showed that the NO conversion reaches a maximum at a certain temperature and then decreases with increasing temperature (Fig. 5). The same trend can be traced among zeolite catalysts [5]. It is worthwhile to mention that the NO reduction over In_2O_3–GAZ system was not similar to that exhibited by In_2O_3–GA and In_2O_3–Al_2O_3 systems in the presence of H_2O vapor [3, 15]. Haneda et al. [3] reported that the addition of In_2O_3 into GA enhanced the activity for NO reduction by propene in the presence of H_2O. In contrast, Pitukmanorom and Ying [8] reported that upon addition of In_2O_3 into GA, catalytic activity was not changed significantly. Figure 5 also shows that Mn_2O_3–GAZ catalysts had very poor catalytic activity in the presence or absence of H_2O vapor. A low activity might be due to the presence of large particles of manganese oxide which can oxidize C_2H_4 in the presence of O_2.

In this study, the multi–component spinel catalysts that consist of metal cations and Al_2O_3 oxide matrix (support) was used for the NO reduction by C_2H_4. The matrixes and doped metal cations play crucial role for SCR of NO. In the multi–component catalyst, the added metal cations probably play two important roles: first, they act as active reaction sites over which reaction

intermediates are formed and second they promote the activity of original metal species by influencing the support, metal, or both of them. Shimizu et al. [19] reported that the high activity and selectivity of metal oxide doped−Al_2O_3 were attributed to the presence of surface aluminate phase, which contains transition metal cations evenly distributed in the Al_2O_3 matrix. Previous studies [20, 21] revealed that the surface aluminate phase described as 'surface spinel' forms by calcining transition metal catalysts supported on Al_2O_3 at high temperatures. It seems that the spinel could be formed in the Al_2O_3 support and simple interchange can take place between Al^{3+} ions and metal cations from the metal ions doped-GAZ system. The structure of In_2O_3−GAZ system is not fully understood yet, studies are under way in our laboratory to gain additional insight, and will be reported separately. It has been suggested that the active sites for the hydrocarbons−SCR reaction might be associated with tetrahedral Ga^{3+} ions and with octahedral Al^{3+} ions in the next—nearest—neighbor sites in GA system [5, 6]. The influence of small addition of In_2O_3 into GAZ can be of great significance for shaping the overall properties of the catalytic systems, particularly in the presence of H_2O vapor. It seems that a change in the distribution of the metal ions among tetra− and octrahedral sites of γ-Al_2O_3 might have some positive effect on catalytic activity. It is believed that this remarkable lean−NO_x activity arose in part from the incorporation and/or thin layer of In_2O_3 over GAZ spinel, which might enhance the hydrocarbon oxidation in the presence of H_2O vapor.

Figure 6 depicted C_2H_4 conversion at different temperature on GAZ spinel catalysts in the presence of H_2O. It was found that GAZ shows significant C_2H_4 conversion in the presence of H_2O. The addition of 1 mol% In_2O_3 into GAZ system slightly enhances the catalytic activity in NO conversion. Furthermore, the presence of 1 mol% In_2O_3 led to an increase in C_2H_4 conversion, and complete C_2H_4 conversion was achieved at 500°C. These results show that the selective catalytic reduction of NO is inversely related to the C_2H_4 conversion. Due to the synergism between these oxides components generated on In_2O_3 the activated C_2H_4 species participate in the reduction of NO to N_2 by more selective GAZ and avoid consumption in the combustion process.

A Comparison of Ceramic and Metal Honeycombs

NO reduction performance of cordierite and metal honeycombs washcoated with In_2O_3−GAZ spinel catalysts were investigated to elaborate practical usability of de−NO_x catalyst. Two types of honeycombs and cell designs (circular and square) were used for the de−NO_x performance measurements. Figure 7a shows the cordierite honeycombs with 900 cpsi (number of cells/in²) and circular parallel channels cell type while a magnified image of Fig. 7a is shown in Fig 7b. The thickness of washcoated cordierite honeycomb with circular−
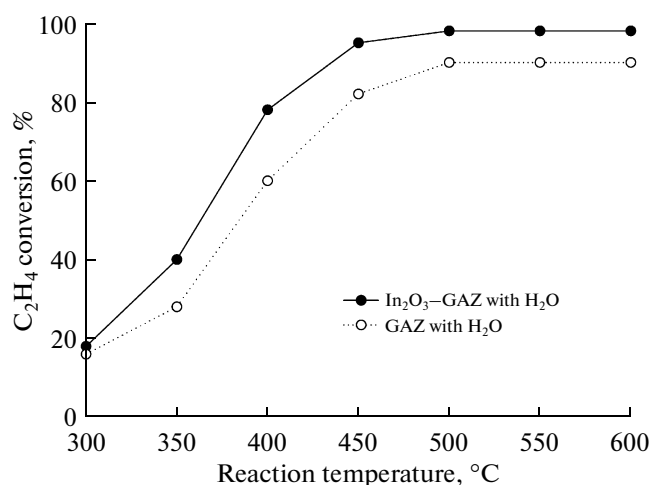
Fig. 6. Conversion of C_2H_4 on the GAZ and GAZ catalysts containing 1 mol% In_2O_3 as a function of the reaction temperature. The reaction conditions are the same as in Fig. 2, GHSV−20000 h^{-1}.

channels was 14 μm. Figure 7c shows the cordierite honeycombs with cell type square channels and its cross-sectional SEM images of one corner of a single square channel (Fig. 7d). The SEM image shows that the washcoat is adhered to the walls of honeycomb (Fig 7d). The thickness of washcoat measured by SEM was found to be 36 μm on the corners, and 16 on the sides. It appeared that corners of the honeycomb particularly those of the square channel type honeycomb accumulate larger amounts of the catalyst. In the case of metal honeycomb, zigzag square channels cell (Fig. 7e and 7f) with 900 cpsi were used. A magnified SEM image of metal honeycomb for sample 7e was registered to visualize the insight properties of the catalysts. However, it was not possible to prepare a small piece of metal honeycomb sample coated with catalysts for SEM image due to its inadequate shape and hardness.

Recently, the selective catalytic reduction of NO_x by propene under lean−burn conditions was investigated over a multi−component system such as Pd−$Ce_{0.66}Zr_{0.34}O_2$−TiO_2−Al_2O_3 catalysts supported on metal honeycomb [22]. However, Pd−$Ce_{0.66}Zr_{0.34}O_2$−TiO_2−Al_2O_3 catalysts did not show any catalytic activity in the presence of H_2O vapor. The dependence of NO and C_2H_4 conversions on temperature was explored for the cordierite (Fig. 8 (a)) and metal honeycombs (Fig. 8b) using 900 cpsi washcoated In_2O_3−GAZ spinel catalyst. The reaction conditions were as follows: NO−1000 ppm, C_2H_4 −2000 ppm, O_2 −10%, SV− 20.000 h$^-$^{1}. The In_2O_3−GAZ spinel catalyst in the wash coated honeycomb exhibited nearly the same temperature dependence of NO and C_2H_4 conversion as In_2O_3−GAZ spinel powders. It is believed that the catalytic activity of the In_2O_3−GAZ spinel powders was not deteriorated by the alumina sol and honeycomb substrate. Temperature dependence of catalytic activity was
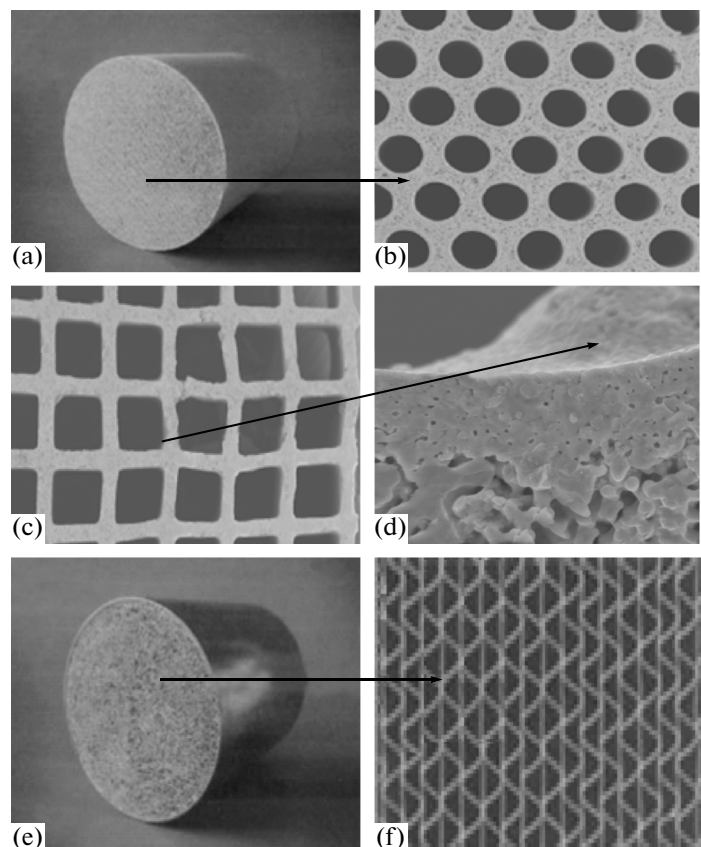
Fig. 7. Image of typical cordierite honeycomb with circular cells (a), a magnified SEM image of the same sample (b), cordierite honeycomb with square cell (c) and its cross-sectional image of one corner of a single square cell (d), metal honeycomb with zigzag square cell (e), and enlarged image of the same sample (f).

found to be almost similar for both the washcoated cordierite and metal honeycombs (Fig. 8). NO conversion over the metal honeycomb catalyst could reach a steady state after 8 min provided that temperature was rapidly increased to the desired temperature within 10 min, and then held constant for 1 h. On the other hand, the NO conversion over the ceramic monolithic catalyst was slowly changed when temperature increases to the desired temperature followed by the stabilization for 30 min. It is well known that due to a high thermal conductivity of the metal substrate a radial heat transfer coefficient in the catalytic bed arises that can not be recorded under the same condition when cordierite is used. Since metal honeycomb was made of stainless steel, the catalysts supported on metal honeycomb could be warmed quickly to reach ambient temperature. It might be effective for quick start−up of de−NO$_x$ reactor using metal honeycomb.

Durability of Honeycomb Catalyst Washcoated with In$_2$O$_3$-GAZ

Exhaust gases usually contain materials that are poisonous to the catalysts, such as H$_2$O vapor and SO$_2$. The reaction inhibition and poisoning of the catalysts by these compounds are important issues to be addressed. However, in many cases the catalytic activity decreased monotonously or drastically with time in the presence of H$_2$O vapor and SO$_2$. In this study, the metal honeycomb was washcoated with In$_2$O$_3$−GAZ and the catalytic durability tests were performed in the presence of H$_2$O vapor and SO$_2$. When H$_2$O vapor (10%) and SO$_2$ (3 ppm) was added to 100 ppm NO, 2000 ppm C$_2$H$_4$, and 10% O$_2$ containing system, the conversion of NO into N$_2$ decreased from 78% (without H$_2$O vapor) to 69% at 500°C. Afterwards, stable NO conversion was observed for more than 100 hrs (Fig. 9). It was observed that this effect was fully reversible; the conversion was reduced in presence but restored in the absence of H$_2$O and SO$_2$. Upon addition of 3 ppm SO$_2$, the activity of In$_2$O$_3$−GAZ was not changed. However, when concentration of SO$_2$ increased to 90 ppm the activity started to decrease.

The In$_2$O$_3$−GAZ spinel composite catalyst is active in the NO reduction in H$_2$O + SO$_2$ + O$_2$ steam flow, and displays no sign of performance degradation for more than 100 hrs. High catalytic activity of In$_2$O$_3$−GAZ was attributed to the spinel−type structure with an appropriate amount of acid−base sites, which might enhance the hydrocarbon conversion. The catalytic activity of
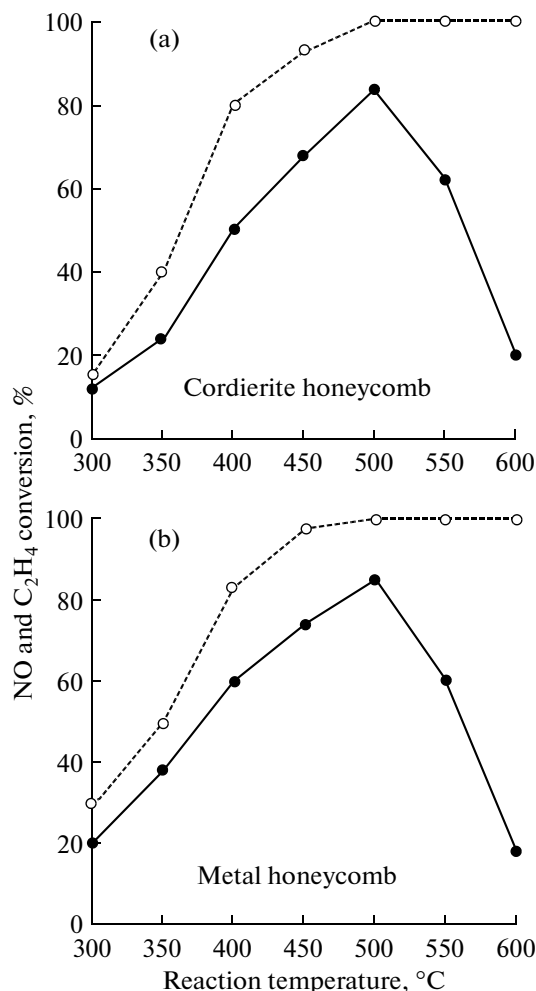
Fig. 8. Conversions of NO and C_2H_4 as a function of the reaction temperature for cordierite (a) and metal honeycomb washcoated with the GAZ spinel catalyst doped with In_2O_3. The reaction conditions are the same as in Fig. 2(a); GHSV–20000 h^{-1}. Symbols ● and ○ indicate conversion of NO and C_2H_4, respectively.
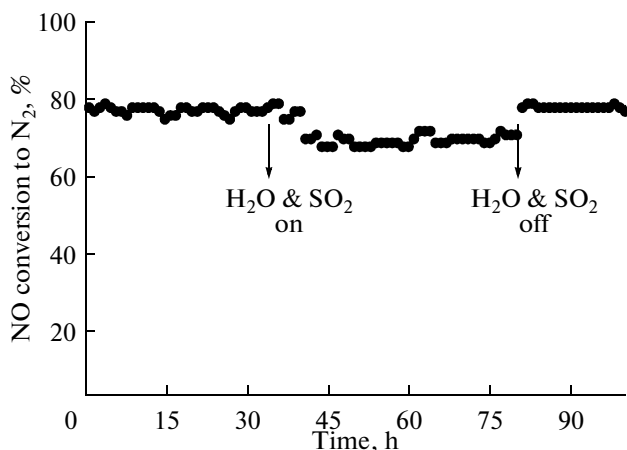
Fig. 9. Stability of catalytic activity in the presence of H_2O vapor and SO_2 over In_2O_3–GAZ/metal honeycomb with cell size 900 cpsi at 500°C. Feed composition: NO–1000 ppm, C2H4–2000 ppm, O2–10%, H_2O vapor–10%, SO_2–3 ppm, He as diluent. SV–20000 h^{-1} at 500°C.

both the wash–coated cordierite and metal honey-combs is not impaired by alumina sol and honeycomb substrate. The durability of the In_2O_3–GAZ spinel catalyst was found to be very high even in the washcoated 1 honeycomb.

REFERENCES

1. Luo, Y.M., Hao, J.M., Hou, Z.Y., Fu, L.X., Li, R.T., Ning, P., and Zheng, X.M., *Catal. Today*, 2004, vol. 93, p. 797.
2. Iwamoto, M. and Hamada, H., *Catal Today*, 1991, vol. 10, p. 57.
3. Haneda, M., Kintaichi, Y., and Hamada, H., *Catal. Lett.*, 1998, vol. 55, p. 47.
4. Serban, M., Halasz, I., and Datta, R., *Catal. Lett.*, 1999, vol. 63, p. 217.
5. Zahir, M.H., Katayama, S., and Awano, M., *Catal. Lett.*, 2004, vol. 93, p. 145.
6. Zahir, M.H., Katayama, S., and Awano, M., *Mater. Chem. Phys.*, 2004, vol. 86, p. 99.
7. Zahir, M.H., *Mater. Chem. Phys.*, 2011, vol. 130, p. 1038.
8. Pitukmanorom, P. and Ying, J.Y., *Nanotoday*, 2009, vol. 4, p. 220.
9. Kašpar, J., Fornasiero, P., and Hickey, N., *Catal. Today*, 2003, vol. 77, p. 419.
10. Shelef, M., *Chem. Rev.*, 1995, vol. 95, p. 209.
11. DeLuca J.P. and Campbell, L.E., in *Advanced Materials in Catalysis*, Burton, J.J. and Garten, R.L., Eds., New York: Academic, 1977, p. 293.
12. Choi, H., Ham, S.W., Nam, I.S., and Kim, Y.G., *Ind. Eng. Chem. Res.*, 1996, vol. 35, p. 106.
13. Kaltner, W., Veprek-Heijman, M., Jentys, A., and Lercher, J.A., *Appl. Catal., B*, 2009, vol. 89, p. 123.
14. Haneda, M., Kintaichi, Y., Mizushima, T., Kakuta, N., and Hamada, H., *Appl. Catal., B*, 2001, vol. 31, p. 81.
15. Tang, X., Hao, J., Xu, W., and Li, J., *Catal. Commun.*, 2007, vol. 8, p. 329.
16. Smirniotis, P.G., Sreekanth, P.M., Pen, D.A., and Jenkins, R.G., *Ind. Eng. Chem. Res.*, 2006, vol. 45, p. 6436.
17. Perdigon-Melon, J.A., Gervasini, A., and Auroux, A., *J. Catal.,* 2005, vol. 234, p. 421.
18. Li, J., Hao, J., Cui, X., and Fu, L., *Catal. Lett.*, 2005, vol. 103, p. 75.
19. Shimizu, K., Satsuma, A., and Hattori, T., *Appl. Catal., B*, 1998, vol. 16, p. 319.
20. Friedman, R.M., Freeman, J.J., and Lytle, F.W., *J.* 2 *Catal.*, 1978, vol. 55, p. 10.
21. Chin, R.L. and Hercules, D.M., *J. Phys Chem.*, 1982, vol. 86, p. 360.
22. Hong, S., Yaobin, Z., Xie, Q., Shuo, C., Zhenping, Q., and Yunlong, Z., *Catal. Today*, 2008, vol. 139, p. 130.

SPELL: 1. washcoated