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KGa-priderite and related compound for the selective reduction of nitrogen monoxide with propylene

T. MORI, S. YAMAUCHI, H. YAMAMURA
TOSOH Corporation, Tsukuba Research Laboratory, Miyuki-gaoka 43, Tsukuba, Ibaraki 305, Japan

M. WATANABE
National Institute for Research in Inorganic Materials, Namiki 1-1, Tsukuba, Ibaraki 305, Japan

The catalytic activity of KGa-priderite, $K_{1.6}Ga_{1.6}Ti_{6.4}O_{16}$, and its related compound $KGa_8Ga_9Ti_{15}O_{56}$ was investigated for the selective reduction of nitrogen monoxide (NO) with propylene (C_3H_6) in the presence of high oxygen concentrations. The KGa-priderite showed significant activity during this reaction, but the related compound showed only a little activity. These compounds are quite different from the conventional catalysts for NO_x selective reduction and are characterized by the fact that their properties are free from the effects of solid acidity and support metals. This difference was attributable to the NO desorption rate at the surface of these compounds. It has become clear that the KGa-priderite catalyst remarkably adsorbed NO, and it is suggested that the amount of NO adsorbed and the amount of catalytic activity are able to be increased by the design of priderite structure.

1. Introduction

The selective reduction of nitrogen oxides with hydrocarbons in an oxidizing atmosphere has recently become of great interest. Iwamoto *et al.* found that the selective reduction of nitrogen monoxide (NO) occurred very effectively on Cu–ZSM-5 and related metal zeolites [1–4]. Hamada *et al.* revealed that such a catalytic reduction of NO could take place effectively even on the H-form of zeolite and transition metal-promoted silica or alumina catalysts [5–8].

Priderites have the hollandite-type one-dimensional tunnel structure. The priderite-type unit cell is illustrated in Fig. 1, and it has usually a tetragonal symmetry. The tunnels, which are occupied by alkaline or alkaline-earth ions, have been well studied as one-dimensional ion-conduction paths [9]. $K_{1.6}Ga_{1.6}Ti_{6.4}O_{16}$ (KGTO) is one of the priderite-type compounds [10]. The related compound, $KGa_8Ga_9Ti_{15}O_{56}$ (KGGTO), has an intergrowth structure of rutile and β-gallia and also contains one-dimensional tunnels of different types. The crystal structure of KGGTO is illustrated in Fig. 2. The tunnels in KGGTO are as large as 0.34–0.36 nm in free diameter [11–14].

In this work, priderite was proposed as a new type of catalyst for the selective reduction of NO with propylene. Moreover, the well-crystallized catalysts were used to clarify the active site, and the mechanism of this selective reduction of NO and the possibility of designing the catalytic reaction were discussed.

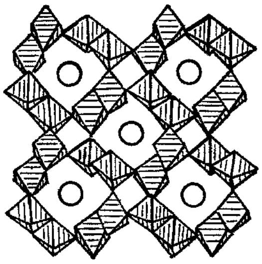

Figure 1 The crystal structure of priderite-type compound.

2. Experimental procedure

Priderites KGTO, $Rb_{1.4}Ga_{1.4}Ti_{6.6}O_{16}$ (RGTO) and the related compound KGGTO were prepared by calcining starting mixtures. The starting materials used were titanium oxide TiO_2 (WAKO Pure Chemical Industries, 99.99% pure, Japan), gallium oxide Ga_2O_3 (WAKO Pure Chemical Industries, 99.99% pure, Japan), potassium carbonate (WAKO Pure Chemical Industries, special grade, Japan) and rubidium carbonate (WAKO Pure Chemical Industries,

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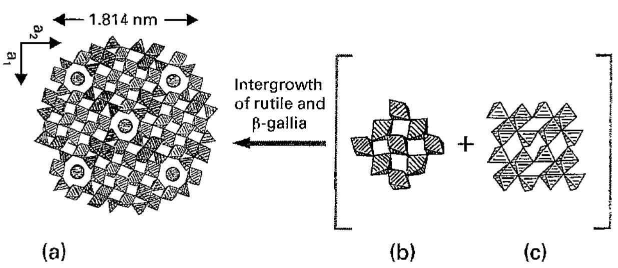

Figure 2 The crystal structure of KGGTO in (a) the (0 0 1) projection and the structural elements of (b) rutile and (c) β-gallia.

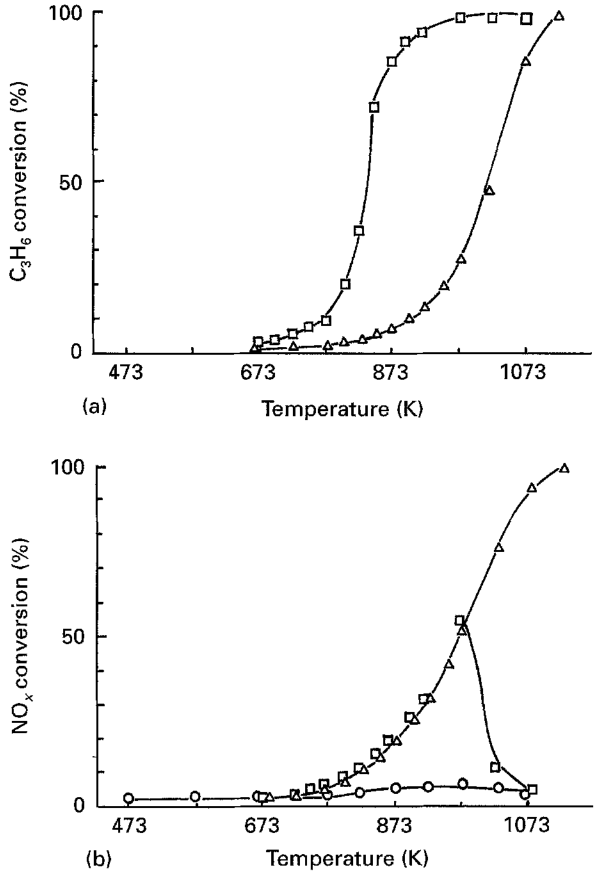

Figure 3 The temperature-dependence curves of (a) C_3H_6 and (b) NO_x conversions on KGTO catalyst. (○) NO, (△) NO + C_3H_6, (□) NO + C_3H_6 + O_2.

special grade, Japan). These starting materials were mixed at the stoichiometric molar ratios of KGTO, RGTO and KGGTO. The mixtures were calcined at 1223 K for 1 h and then at 1473–1573 K for 4 h. The surface area values of these products were from 1–2 $m^2 g^{-1}$. These products were single phase. The samples were used as the catalyst without catalyst supports for selective reduction of NO with C_3H_6. The reaction was carried out in a flow reactor equipped with a quartz cell containing the catalyst, by passing a mixed gas of NO (1200 p.p.m.), oxygen (4%) and C_3H_6 (800 p.p.m.) in helium at a space velocity of 2500 h^{-1}. The effluent gas was analysed by gas chromatography with a Porapak Q column (for nitrous oxide, carbon dioxide and propylene) and a NO_x meter. The NO_x meter can detect NO and nitrogen dioxide (NO_2) as NO_x. The catalytic activity for NO_x reduction was evaluated by the conversion of NO + NO_2 because the formation of nitrous oxide was negligible in all cases. The amounts of desorbed NO or desorbed NH_3 from the priderites and the related compound were examined by means of a temperature-programmed desorption method (NO-TPD, NH_3-TPD).

3. Results and discussion

Fig. 3 shows the temperature-dependence curves of catalytic activities of KGTO under three kinds of atmosphere (NO, NO + C_3H_6 and NO + C_3H_6 + O_2). KGTO catalyst was inactive in an atmosphere of NO alone, and hence it does not make a contribution to the direct decomposition of NO. However, the KGTO catalyst in the NO + C_3H_6 atmosphere was remarkably active and the conversion of NO_x increased with increasing propylene content. Therefore, this reaction of the priderite can be regarded as the selective reduction of NO by the assistance of propylene. The maximum NO_x conversion of KGTO was 60% at 973 K for the selective reduction of NO with C_3H_6 in an atmosphere of highly concentrated oxygen.

The temperature-dependence curves in Fig. 4 show the conversion behaviour of C_3H_6 and NO_x on RGTO catalyst measured in NO, NO + C_3H_6 and

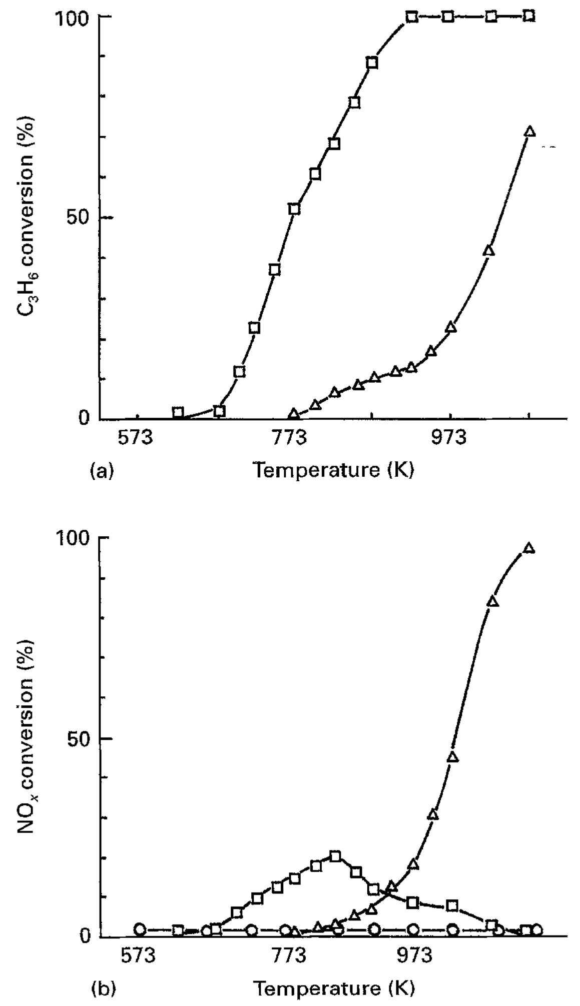

Figure 4 The temperature-dependence curves of (a) C_3H_6 and (b) NO_x conversions on RGTO catalyst. (○) NO, (△) NO + C_3H_6, (□) NO + C_3H_6 + O_2.

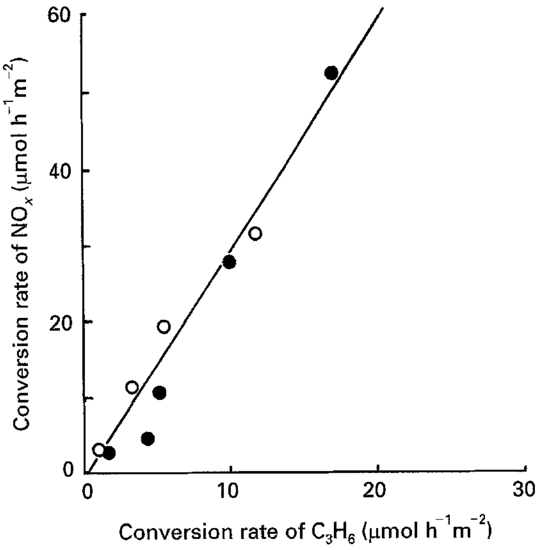

Figure 5 Conversion rate of NO$_x$ as a function of conversion rate of C$_3$H$_6$. (●) RGTO catalyst, (○) KGTO catalyst.

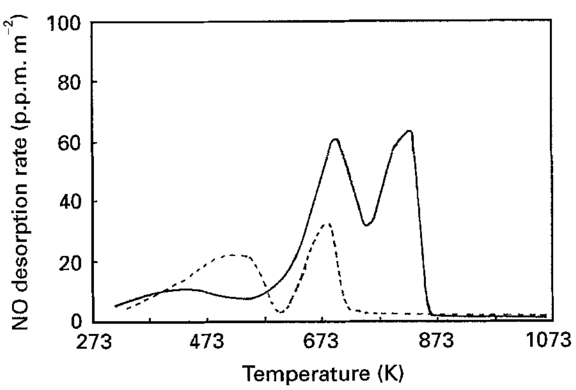

Figure 6 NO-TPD curves of (—) KGTO and (···) RGTO catalysts.

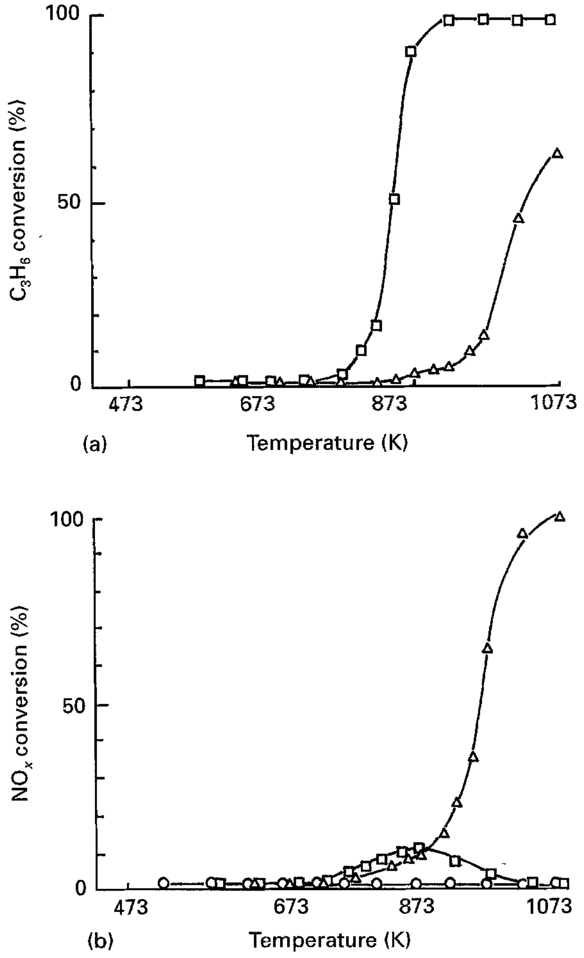

Figure 7 The temperature-dependence curves of (a) C$_3$H$_6$ and (b) NO$_x$ conversions on KGGTO catalyst. (○) NO, (△) NO + C$_3$H$_6$, (□) NO + C$_3$H$_6$ + O$_2$.

NO + C$_3$H$_6$ + O$_2$, where RGTO is the rubidium derivative of KGTO. The RGTO catalyst was also inactive with NO alone. However, it selectively reduced NO with the assistance of propylene. In the presence of highly concentrated oxygen, the maximum NO$_x$ conversion rate of RGTO was 20% at 873 K. This rate is lower than that of KGTO. In order to consider the reaction mechanism of the selective reduction of NO with propylene, the elementary reaction (NO + C$_3$H$_6$) was investigated. In Fig. 5, the conversion rate of NO$_x$ is plotted as a function of that of C$_3$H$_6$. The relation in the conversion rate between NO$_x$ and C$_3$H$_6$ was linear at the initial stage of these reactions. The gradient of this line was about 3 and the same for KGTO and RGTO. Therefore, the reaction mechanism would be the same between them. It is suggested from this gradient value that the model reaction (Reaction 1) proceeds in the initial stage of the NO + C$_3$H$_6$ reaction on the priderites, and that the partial oxidation of C$_3$H$_6$ by NO was a dominant factor in this reaction

$$6\,NO + 2\,C_3H_6 \rightarrow 3\,N_2 + 6\,CO + 6\,H_2$$

$$(NO/C_3H_6 \text{ value} = 3) \quad (1)$$

In order to discuss the difference of NO$_x$ conversion between KGTO and RGTO, the measurements of NO–TPD were performed. As shown in Fig. 6, the NO desorption rate of KGTO has two sharp peaks: one around 673 K and the other around 823 K. The adsorbed amount of NO, calculated from the area under the NO–TPD curve, is 8.8 μmol m^{-2}. On the other hand, the desorption rate of NO on RGTO consists of two small peaks which are positioned at 673 K and around 523 K. The broad peak at 523 K was attributed to physical adsorption of NO. The area of the sharp peak at 673 K corresponds to 1.7 μmol m^{-2}. The difference in NO$_x$ conversion between KGTO and RGTO resulted from the amount of NO adsorbed on the surface of the catalyst. It is expected from the substitution effect of tunnel ions, that the potassium ion may make a preferable contribution to the adsorption of NO molecules on the priderite surface through an electric correlation with NO$^-$ species. Such a feature, however, seems to depend not only on the ionic species in the priderite-type framework but also on other factors such as the effects of solid acidity, support metals and the type of crystal structures. The catalytic activities of the related compound KGGTO were also investigated in order to estimate the effect of the type of crystal structure.

Fig. 7 shows the temperature dependence of catalytic activities of the related compound KGGTO in the atmospheres of NO, NO + C$_3$H$_6$ and NO + C$_3$H$_6$ + O$_2$. In this figure, it was found that KGGTO is slightly active in NO selective reduction

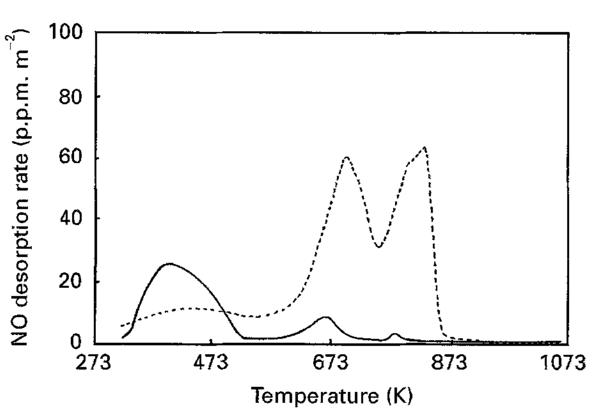

Figure 8 NO-TPD curves of (—) KGGTO and (···) KGTO catalysts.

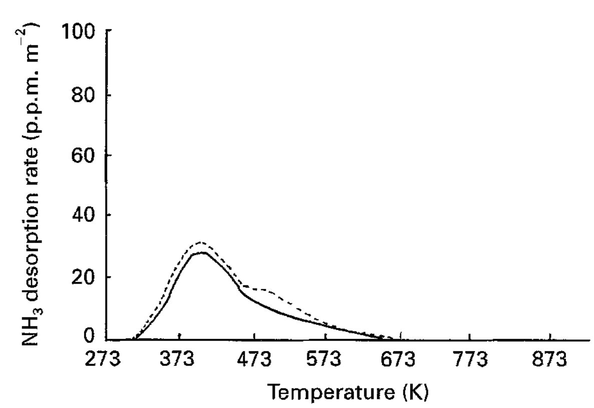

Figure 10 NH_3–TPD curves of (—) KGGTO and (···) KGTO catalysts.

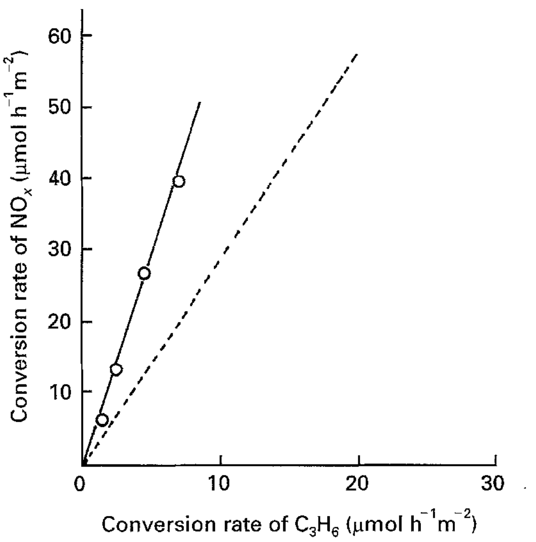

Figure 9 Conversion rate of NO_x as a function of conversion rate of C_3H_6. (O) KGGTO catalyst, (···) priderite line (reference to Fig. 5).

under the coexistence of oxygen. The difference in activity between this compound and KGTO became clear by comparing the NO–TPD behaviour shown in Fig. 8.

The NO desorption rate of KGGTO is very small in comparison with that of KGTO, and the amount of NO adsorbed on KGGTO is 0.48 μmol m^{-2}. Such a low adsorption capacity of NO can explain the low activities of the KGGTO catalyst. In Fig. 9, the conversion rate of NO_x is plotted as a function of that of C_3H_6 for KGTO and KGGTO catalysts. The relation of the conversion rate between NO_x and C_3H_6 was linear during the initial stage of these reactions. The gradient of this line was about 6 for KGGTO, but was not the same between KGTO and KGGTO. From these results, it is suggested that their reaction mechanisms differ, and the electric correlation between the NO^- species on the framework of priderite and the tunnel ions in it was stronger than that of KGGTO. Therefore, it is speculated that the framework of priderite-type structure played an important role in the electric correlation and contributed to the increase of catalytic activity.

In order to investigate the influence of solid acidity, measurements of NH_3–TPD for KGTO and KGGTO were performed and the results are shown in Fig. 10. If there were acidic points on the catalyst surface, the peak should appear above 573 K (chemical adsorption region). Their NH_3–TPD all have one peak; however, these peaks were positioned around 473 K and were attributed to physical adsorption of NH_3. Therefore, the effect of solid acidity in this study was negligible. Furthermore, well-crystallized single-phase samples were used and it was considered that the effect of free support metals was also negligible. As a result, it can be expected that the effect of crystal structure was a dominant factor of this reaction. Moreover, it is speculated that the activity of this catalytic reduction can increase by means of selection of the tunnel ions and design of a framework of one-dimensional tunnel structure.

4. Conclusions

The catalytic properties of priderites and the related compound were studied for the selective reduction of NO with propylene in the presence of highly concentrated oxygen.

1. KGTO showed significant catalytic activity for the selective reduction of NO with C_3H_6. RGTO, isostructural to KGTO and containing rubidium in the tunnel instead of potassium, exhibited the same reduction behaviour as KGTO. It was suggested that these priderites gave the same reduction mechanism.
2. KGTO has a high adsorptive capacity for NO, which is closely connected to significant activity.
3. The priderite-related compound, KGGTO, had virtually no significant activity for NO selective reduction. The difference in activity between priderites and their related compound was attributable to the NO adsorptive capacity.

Therefore, it was speculated that selection of the tunnel ions and design of a framework of one-dimensional tunnel structure contributed to the increase in the amount of NO adsorbed and an increase in the activity of this catalytic reduction. The conversion values of KGa-priderite catalyst are relatively smaller than those of the known catalysts for NO_x selective reduction, but it should be noted that the specific surface area of the present material (1–2 m^2 g^{-1}) is very much lower than that previously known (a few tens to hundreds $m^2 g^{-1}$). Therefore, it can be expected that the excellent activity in this catalytic reduction is given by the designing of a framework of the priderite-type compound and the preparation of samples with a high surface area.

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