Partial oxidation of propene over metal oxide catalysts pretreated with NO_2

Atsushi Ueda[a,*], Kazuyuki Ejima[b], Masashi Azuma[b] and Tetsuhiko Kobayashi[a]

[a] *Osaka National Research Institute, AIST, Midorigaoka 1-8-31, Ikeda, Osaka 563-577, Japan*
E-mail: ueda@onri.go.jp
[b] *Department of Applied Chemistry, Osaka Institute of Technology, Omiya 5, Asashi-ku, Osaka 535-0002, Japan*

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Titania pretreated with NO_2 has been found to catalyze the partial oxidation of propene into oxygenates such as acetone and acrolein at around 623 K, while fresh TiO_2 produces only carbon oxides. Temperature-programmed desorption (TPD) revealed that nitrogen oxides adsorbed on TiO_2 are stable at temperatures below 673 K. Even after the propene oxidation at 573 K for 2 h, nitrogen oxides were confirmed still to exist on the TiO_2 surface. At temperatures higher than 673 K, however, the desorption and/or the reduction of the adsorbed nitrogen oxides took place, and concomitantly the catalytic ability giving oxygenates disappeared.

Keywords: nitrogen dioxide, titania, propene, selective oxidation, adsorption

1. Introduction

The catalytic behavior of nitrogen oxides (NOx) adsorbed on solid surfaces has been attracting interest in the catalysis research [1–7] and, also, in the gas sensor research [8]. In their study of the catalytic NOx reduction by methane, Armor et al. [1,2] have proposed that nitrogen dioxide (NO_2) adsorbed on Co/zeolite provides the sites activating methane. Such a role of adsorbed NO_2 in the catalytic NOx reduction has been accepted by other investigators [3,6]. Recently, Ando et al. [8] have found in the study of CO gas sensors that a pretreatment of gas-sensitive material, i.e., NiO, with NO_2 brings about an appreciable enhancement of the CO sensitivity. A redox cycle between adsorbed NO_2 and NO_3 on NiO has been postulated to facilitate the oxidation of CO on the surface and, hence, the CO sensitivity [8].

In order to obtain higher yields of oxygenates, addition of NOx to the reactant gas mixture has been widely attempted in gas-phase reactions between hydrocarbons and oxygen [9,10]. Recently, Otsuka et al. [11] have claimed that a redox cycle between NO and NO_2 in the gas phase plays a catalytic role in the oxygenate formation from light alkanes. In contrast to a number of publications regarding the NOx-promoted partial oxidation of hydrocarbons in gas phase, the contribution of NOx adsorbed on metal oxide catalysts toward the hydrocarbon oxidation is still unclear at present. In the present study, we have examined the catalytic behavior of metal oxides pretreated with NO_2 in the oxidation of propene. Stability of the adsorbed NO_2 is also discussed.

2. Experimental

The following metal oxides were used as catalysts: MgO (Ube Industries, specific surface area of 100 $m^2\,g^{-1}$), ZnO (Toyo CCI Co., Ltd., specific surface area of 57 $m^2\,g^{-1}$), ZrO_2 (Japan Aerosil Co., Ltd., specific surface area of 75 $m^2\,g^{-1}$), TiO_2 (P-25, Japan Aerosil Co., Ltd., specific surface area of 50 $m^2\,g^{-1}$), γ-Al_2O_3 (AKP-G015, Sumitomo Chemical Co., Ltd., specific surface area of 184 $m^2\,g^{-1}$), and SiO_2 (Merk Co., Ltd., specific surface area of 400 $m^2\,g^{-1}$).

Catalytic activity measurements were carried out by using a fixed-bed flow reactor. A sample (200 mg) was placed in a quartz tube, heated to 573 K in 30 min in a stream of He at a flow rate of 50 $cm^3\,min^{-1}$, and then was kept at 573 K for 30 min. Adsorption of NO_2 on metal oxides was carried out by passing 2 vol% NO_2 in a He background at a flow rate of 50 $cm^3\,min^{-1}$ at 573 K for 3 h. Then, pure He gas was passed through the catalyst bed for 10 min at 573 K to remove NO_2 from the gas phase in the reactor. The reactant gas mixture containing 20 vol% C_3H_6, 16 vol% O_2 in a He background (without NO_2) was passed through the catalyst bed at a flow rate of 50 $cm^3\,min^{-1}$. The catalyst temperature was monitored with a quartz-tube-covered thermocouple contacting with the inlet part of the catalyst bed and was raised stepwise and maintained for 2 h at each temperature.

Reactants and products were analyzed with three gas chromatographs (GCs) and a NOx analyzer. Oxygen, nitrogen, methane, and carbon monoxide were analyzed by a GC (Shimadzu GC-14B) equipped with a thermal conductivity detector (TCD) and a molecular sieve 13X column (5 m) kept at 373 K. Carbon dioxide and nitrous oxide (N_2O) were analyzed by a GC (Yanaco G-2800) equipped with TCD

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[*] To whom correspondence should be addressed.

and a column of active carbon (3 m) kept at 373 K. Carbon monoxide, carbon dioxide, C1–C3 hydrocarbons, and C1–C3 oxygenates such as acetone, 2-propanol, acrolein, acrylic acid, etc. were analyzed by a GC (Shimadzu GC-14B) equipped with a methane converter and a flame ionization detector (FID) and a Porapak Q column (3 m). Nitrogen monoxide (NO) and nitrogen dioxide (NO_2) were analyzed with a chemiluminescent NOx analyzer (Yanaco CLS-88US). The minimum detectable amounts of NO and of NO + NO_2 were 0.1 ppm, and the concentrations of both NO and NO_2 could be determined within an error of 1%. The minimum detectable amount for N_2O was 10 ppm. A GC mass spectrometer (Hewlett Packard HP5971A/GCD) was also used to identify C1–C3 oxygenates.

Temperature-programmed desorption (TPD) of nitrogen oxides adsorbed on TiO_2 was carried out in a helium atmosphere by using an automatic TPD analyzer (Bell Japan, Inc., TPD-43) equipped with a quadrupole mass spectrometer. Adsorption of NO_2 was conducted by passing 2 vol% NO_2 in a He background at a flow rate of 50 $cm^3\,min^{-1}$ at 573 K for 12 h. Desorption was carried out by passing He carrier at a flow rate of 50 $cm^3\,min^{-1}$ at a heating rate of 10 $K\,min^{-1}$.

3. Results and discussion

3.1. Formation of oxygenates over NO_2-treated metal oxides

The oxidation of propene was performed over a fresh TiO_2 catalyst and TiO_2 pretreated with NO_2. Figure 1 shows the distribution of the products from propene as a function of the reaction temperature. The TiO_2 catalyst without NO_2 treatment afforded the formation of CO and CO_2 at temperatures from 523 to 623 K. No oxygenates were detected under the present reaction conditions. On the other hand, appreciable amounts of oxygenates were produced when the NO_2-treated TiO_2 was used as the catalyst. It should be noted that NO_2 is not co-fed into the reactant gas mixture. Acetone exhibited the highest yield among the oxygenates produced. A cracking product of propene, i.e., ethene, was also detected.

Table 1 shows the product selectivities in the propene oxidation over several metal oxides pretreated with NO_2. It seems that basic oxides afford a higher conversion of propene. The quantity of NO_2 adsorbed on basic sites might be related to the catalytic activity. Relatively high yields of oxygenates were obtained when MgO, ZrO_2, or TiO_2 was used as the catalyst after the NO_2 treatment. Without NO_2 treatment these oxides afforded mainly CO and CO_2. NO_2-treated TiO_2 seems favorable for the formation of acrolein and acrylic acid, but strong basicity in the other catalysts may suppress the formation of these compounds.

3.2. Stability of NO_2 adsorbed on TiO_2

Thermal stability of the adsorbed NO_2 on TiO_2 was examined by temperature-programmed desorption (TPD). Figure 2 shows the TPD profile of NO_2 adsorbed on TiO_2. Desorptions of NO and NO_2 were remarkable at around 773 K. The quantity of desorbed NO was three times higher than that of NO_2. This is probably because NO is thermodynamically more stable than NO_2 at these temperatures [12].

The stability of the catalytic property of the NO_2-treated TiO_2 producing oxygenates from propene has been tested at two different temperatures. Figure 3 shows the product distribution in the propene oxidation at 573 K (a) and 673 K (b) as a function of time on stream. As shown in fig-

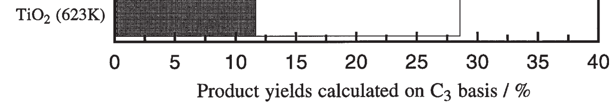

Figure 1. Product distribution in oxidation of propene over NO_2-treated and NO_2-free TiO_2. (a) Acrylic acid; (b) acrolein; (c) 2-propanol; (d) acetone; (e) ethene; (f) carbon dioxide; (g) carbon monoxide.

Table 1
Products selectivities in partial oxidation of propene over metal oxides treated with NO_2.[a]

Catalyst	Temp. (K)	Conv. of C_3H_6 (%)	Selectivity (%)						
			CO	CO_2	C_2H_4	acetone	2-propanol	acrolein	acrylic acid
NO_2/MgO	523	14.7	27.9	31.1	5.5	19.7	12.3	2.8	0.5
NO_2/ZnO	573	15.4	41.6	40.2	5.4	7.8	2.6	0.3	0.1
NO_2/ZrO_2	573	14.8	23.0	38.5	7.4	16.9	9.4	2.1	0.9
NO_2/TiO_2	573	13.4	24.1	10.1	12.8	28.5	4.6	10.8	8.9
NO_2/Al_2O_3	573	8.4	51.2	46.4	0.4	1.2	<0.1	<0.1	<0.1
NO_2/SiO_2	623	1.2	45.0	19.4	<0.2	12.2	10.5	5.4	<0.5
TiO_2	573	3.2	75.1	24.8	<0.1	<0.1	<0.1	<0.1	<0.1

[a] Reaction gas: 20 vol% C_3H_6 and 16 vol% O_2 in a He background at a space velocity of 15,000 h^{-1} ml g-catalyst^{-1}.

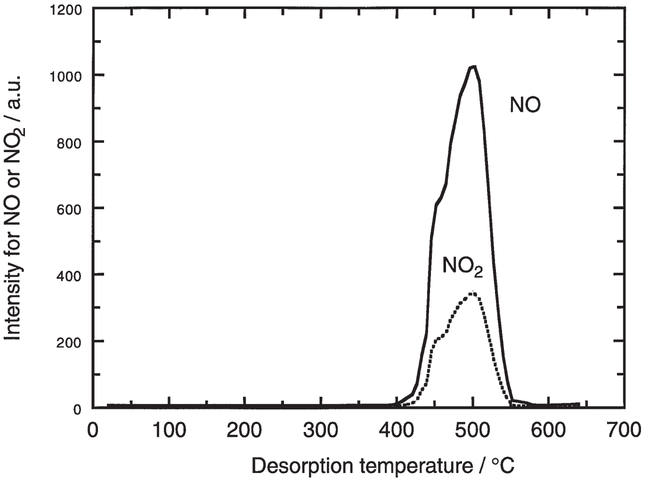

Figure 2. The spectrum of temperature-programmed desorption of NO and NO_2 from NO_2-treated TiO_2.

ure 3(a), yields of the products are almost constant at least for 2 h at 573 K. During the course of the reaction, no compounds containing nitrogen atoms were detected by the GCs and the NOx analyzer employed in the present study. Turnover number of the reaction toward the adsorbed NO_2 can be calculated to be more than 600 times, based upon the amount of NO_2 adsorbed (calculated from the data shown in figure 2) and the integrated amount of the products during the 2 h reaction (figure 3(a)).

After the reaction test at 573 K for 2 h, the reactant gas mixture was switched to the He flow and the temperature of the catalyst bed was raised. At temperatures higher than 700 K, evolution of NO and NO_2 from the catalyst was detected. These results strongly suggest that the propene oxidation at 573 K proceeded over TiO_2 covered with nitrogen oxides, which did not act as a stoichiometric oxidizing agent to propene.

In the reaction at 673 K, however, the catalytic ability to produce oxygenates disappeared gradually after about 60 min of reaction (figure 3(b)). This temperature is equivalent to the onset of the thermal desorption of nitrogen oxides from TiO_2 (figure 2). After 120 min from the beginning of the reaction, the catalysis of the NO_2-treated TiO_2 became almost the same as that of fresh TiO_2, which produces only CO and CO_2. Although no nitrogen oxides were detected during the reaction at 673 K, nitrogen (N_2) was evolved in the period when the gradual change in the catalysis was observed; i.e., after 60 to 120 min during the reaction. Reductive desorption of the adsorbed NO_2 as N_2 might cause the disappearance of the catalytic property producing oxygenates from propene. This is consistent with the fact that the NOx reduction by propene over simple TiO_2 catalyst proceeds at temperatures higher than 673 K [13].

The role of adsorbed NO_2 in the partial oxidation of propene is not clear at present. The radical nature of adsorbed NO_2 [2] may activate propene. It is also plausible that a redox cycle such as NO/NO_2 [2,11] or NO_2/NO_3 [8] on the metal oxides provides mono-oxygen species suitable for the partial oxidation. The mechanism of the reaction is currently investigated in detail and will be reported in a separate paper.

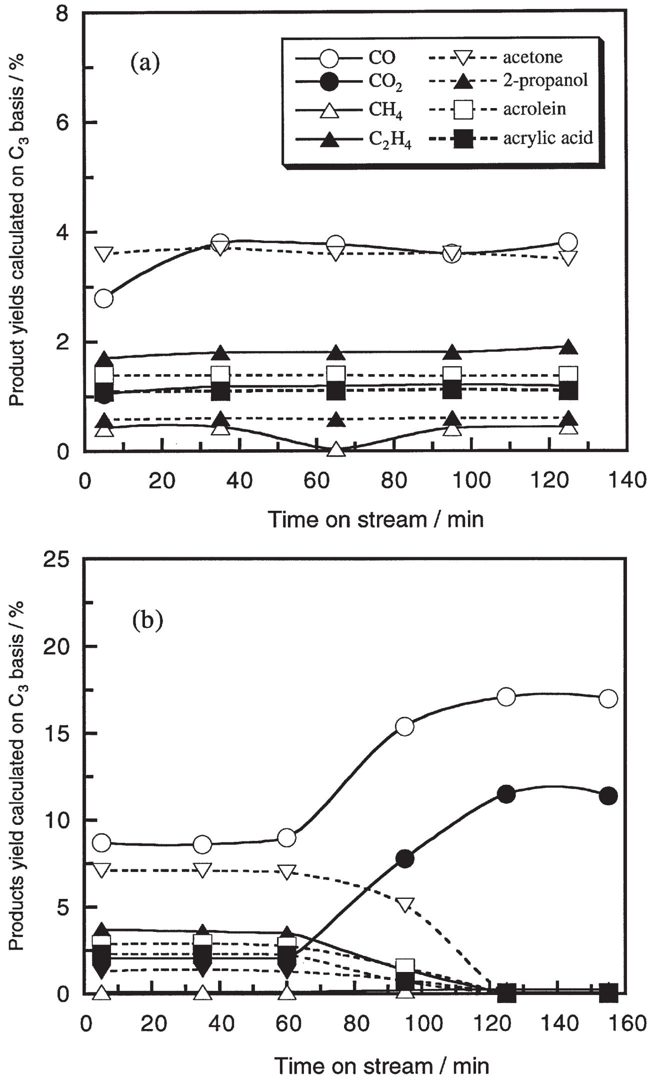

Figure 3. Products distribution as a function of time on stream over NO_2-treated TiO_2. (a) Reaction at 573 K; (b) reaction at 673 K. (○) Carbon monoxide; (●) carbon dioxide; (△) methane; (▲) ethene; (▽) acetone; (▼) 2-propanol; (□) acrolein; (■) acrylic acid.

4. Conclusion

It was found that metal oxides such as TiO_2, MgO, and ZrO_2, pretreated with NO_2, could catalyze the partial oxidation of propene giving oxygenates, while the fresh oxides afforded mainly CO and CO_2. Titania pretreated with NO_2 led to the highest yield of oxygenates among the metal oxides tested. Such a catalytic performance disappeared when the desorption and/or the reduction of adsorbed nitrogen oxides took place at temperatures higher than 673 K. A catalytic role of the adsorbed NOx was proposed.

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