DECOMPOSITION OF NO ON Na^+-MODIFIED MgO EVIDENCED BY ESR AND TEMPERATURE PROGRAMMED DESORPTION (TPD)

Geng ZHANG, Tsunehiro TANAKA, Tsutomu YAMAGUCHI,
Hideshi HATTORI and Kozo TANABE

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060, Japan

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The decomposition of NO to N_2O is accompanied by the formation of O^- over a Na^+-modified MgO surface at moderated temperatures. The importance of the interaction of $(Na^+)_n$ $(n \geq 2)$ clusters and MgO surface is highlighted.

1. Introduction

Direct decomposition of NO to N_2 and O_2 is the most important and efficient process for preventing air pollution from automobile exhaust, in which NO is one of the major components. Extensive investigations [1–5] of this process have been done over a variety of surfaces of transition metals and transition metal oxides. It has been revealed that N_2O is one of the key intermediates. All the investigations also point to the importance of contributions of the transition metal atoms or ions in a redox cycle during the decomposition of NO molecules. Excluding transition metal components, no clear evidence has been demonstrated for NO decomposition to N_2O at moderate temperatures. It is well-known that MgO possesses unique reducing property in addition to its typical basic property [6]. Appropriate modification of the MgO surface is therefore expected to bring about activity for decomposition of NO.

In this paper, we report the decomposition of NO to N_2O and O^- on Na^+-modified MgO (MgO–Na^+) in the temperature range 100–250 °C. Along with a possible mechanism, we propose a structure for the active site for the decomposition of NO over non-transition metal oxides.

2. Experimental

Na^+-modified MgO was prepared by impregnating MgO (Merck) with an aqueous solution of NaOH of known concentrations followed by drying at

120 ° C. The sample was evacuated at 800 ° C to 10^{-4} Torr before use. Three types of Na$^+$–MgO's were prepared and were designated as MgO–Na–0.11, MgO–Na–0.43 and MgO–Na–1.39 which contained 0.11, 0.43 and 1.39 mmol/g of Na$^+$, respectively. Na$^+$-modified Al_2O_3 which contained 0.43 mmol/g of Na$^+$ and designated as Al_2O_3–Na–0.43 was also prepared by impregnating Al_2O_3 (JRC-ALO-4 of the Catalysis Society of Japan) in the same way.

X-band ESR signals were recorded on a JEOL JEX-FE1X spectrometer at room temperature. g values were determined by using Mn^{2+} marker as a reference. TPD experiment was carried out by using a vacuum manifold and at a heating rate of 5 ° C/min, and the desorbed gases were monitored by mass spectrometry. ^{15}NO instead of ^{14}NO was used as an adsorbate to distinguish N_2O and N_2 from CO_2 and CO, respectively, because CO_2 and CO are probable background gases.

3. Results and disussion

Figure 1A shows the ESR spectra obtained after the admission of 10 Torr of NO on MgO–Na–0.43, followed by the successive evacuation at room temperature. A set of signals ($g_{zz} = 2.0028$, $A_{zz} = 39.4G$, $g_{xx} = g_{yy} = 2.0053$) has been assigned to NO_2^{2-} species by Lunsford [7]. The NO_2^{2-} signal drastically di-

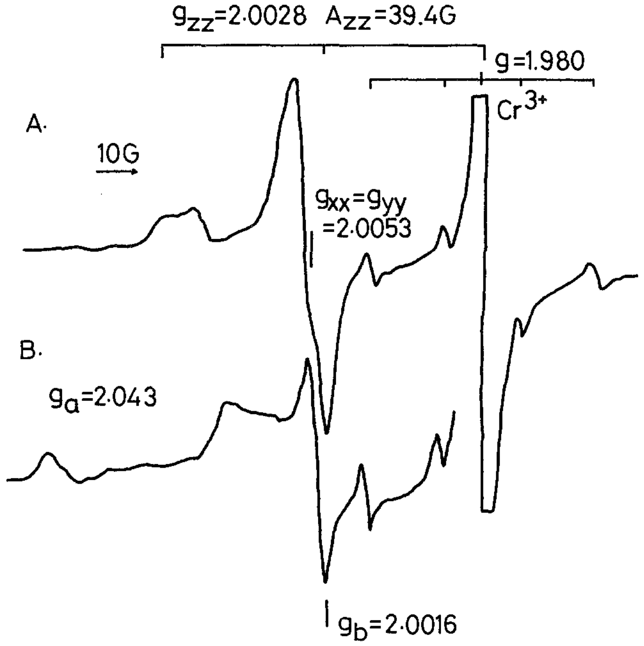

Fig. 1. ESR spectra of MgO–Na$^+$ 0.43 mmol/g evacuated at 800 ° C. A: after NO adsorption at room temperature. B: after evacuation at 250 ° C.

minished after evacuating the sample at 100 °C to 10^{-4} Torr, and completely disappeared at 250 °C. At this temperature, two new signals, (a) and (b), appeared at $g_a = 2.043$ and $g_b = 2.0016$, respectively (fig. 1B). These signals were reproduced in the successive runs carried out after brief evacuation of the used sample at 800 °C. The signals (a) and (b) diminished on heating at 260 °C in the presence of CH_4 or by the evacuation at 400 °C. The signals (a) and (b) were observed only on the MgO–Na–0.43. They were not observed on MgO–Na–0.11 and MgO–Na–1.39. No signals of (a) and (b) were observed on either pure MgO or Al_2O_3–Na–0.43. Another set of strong signals assigned to Cr^{3+} ($g = 1.980$, $A = 17.5G$) [8] impurity in MgO was also observed. This impurity was observed on all the samples examined except Al_2O_3–Na–0.43. However, the signals were not affected by the NO adsorption. Thus the contribution from Cr^{3+} to the signal (a) and (b) or NO_2^{2-} formation could be neglected.

When N_2O was adsorbed on MgO–Na–0.43 followed by the evacuation at 250 °C, signals were obtained with the same g values and similar stability against thermal evacuation and exposure to CH_4. The g values of the signals (a) and (b) are close to those for O^- on MgO produced by thermal quenching in the presence of oxygen [9] or by the reaction of trapped electron with N_2O [10]. It is therefore reasonable to assign them to surface O^- on Na^+-modified MgO. We believe this is the first report on the formation of O^- *via* NO adsorbed on MgO. The NO decomposition is thus expected to occur on MgO–Na–0.43; and this was examined by using temperature programmed desorption (TPD). The result is shown

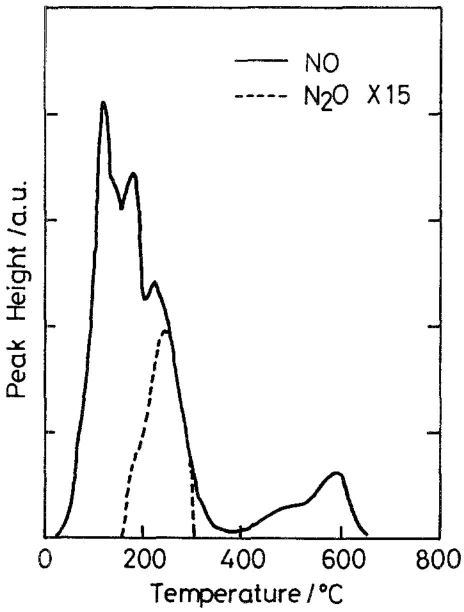

Fig. 2. TPD profiles of NO and N_2O desorbed from MgO–Na$^+$ 0.43 mmol/g.

in fig. 2. N_2O evolved over the range of 100 ° C to 300 ° C, at which the formation of O^- radicals was confirmed by ESR; no N_2 or O_2 was detected probably due to their low yields. The same TPD result was reproduced in the successive runs with the same sample. Desorption of N_2O was not observed on MgO–Na–0.11, MgO–Na–1.39, pure MgO or Al_2O_3–Na–0.43; and no gases other than NO were observed.

An infrared spectroscopic investigation revealed the presence of both $N_2O_2^{2-}$ and NO^- on MgO–Na–0.43 but only NO^- on pure MgO; absorptions at 1317 and 1052 cm^{-1} bands corresponds to the 1314 and 1052 cm^{-1} bands of *cis*-$Na_2N_2O_2$ [11], and the absorption at 1168 cm^{-1} corresponds to NO^- [12]. The bands due to $N_2O_2^{2-}$ vanished after evacuation above 150 ° C. The existence of at least two Na^+ ions adjacent to each other seems favorable for the formation of $N_2O_2^{2-}$. The decomposiiton of $N_2O_2^{2-}$ might produce N_2O and O^- as Na^+–O^- according to equations (1)–(3).

$$NO + e^- \rightarrow NO^- \tag{1}$$

$$2NO^- + 2Na^+ \rightarrow Na–O–N = N–O–Na \tag{2}$$

$$Na–O–N = N–O–Na \rightarrow N_2O + Na^+–O^- + Na^+e^- \tag{3}$$

where e^- stands for the electron from MgO matrix owing to its intrinsic reducing ability. The effect of Na^+ addition on reducing property of MgO will be discussed later.

The presence of two adjacent Na^+ ions or a Na^+ cluster is supported by the following observation. When D_2 was admitted to preadsorbed H_2 on Na^+-modified MgO, TPD confirmed the production of a significant amount of HD, whereas no HD molecule was found on pure MgO. Since the recombination of hydrogen atoms to form an HD molecule requires adjacent sites, this clearly indicates that the sites responsible to the dissociation-recombination of hydrogen molecules are dispersed so sparsely on the pure MgO surface that no H_2–D_2 equilibration reaction takes place [13]. But this is not the case on the Na^+-modified MgO. Introduction of Na^+ to MgO may produce adjacent or cluster sites for hydrogen adsorption around Na^+ ions; and it is likely that the existence of $(Na^+)_n$ $(n \geqq 2)$ cluster plays an important role to facilitate the formation of $N_2O_2^{2-}$ and thus decomposition of NO.

The surface concentration of Na^+ on MgO–Na–0.43 is 2.5% [14] which was confirmed by a quantitative XPS analysis. It has been reported that Na^+ is concentrated on the MgO surface rather than penetrating into the bulk [15], and the value of 2.5% is comparable with the fraction of surface sites on edges and corners of MgO. A low content of Na^+ is not sufficient for the formation of $(Na^+)_n$ $(n \geqq 2)$ cluster, while large amounts of Na^+ may conceal the active portion of MgO matrix for NO adsorption and retard decomposition of NO as demonstrated by the fact that neither N_2O nor O^- were formed on MgO-Na-1.39.

The reducing property of the MgO surface is another important factor for the decomposition of NO as shown in eqs. (1)–(3). It has been reported that the reducing property of MgO is suppressed owing to the doping of Na$^+$ ions [16], and it attains a minimum at about 1.0 mmol/g of Na$^+$ in contrast to the enhancement of basic property of MgO. The fact that MgO–Na–1.39 was inactive to the decomposition is also explained in terms of the suppression of reducing property of MgO due to the addition of large amounts of Na$^+$. The importance of the reducing ability of a catalyst for NO decomposition is also emphasized by the fact that the H_2 preadsorption accelerates formation of N_2O from NO, as described in our previous communication [17]. The fact that no reaction occurred on Na$^+$-modified Al_2O_3 also reveals that it is not Na$^+$ alone, but the cooperative behavior of Na$^+$ and MgO which accelerates the surface reaction.

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