Reactivity of surface isocyanate species with NO, O_2 and NO + O_2 in selective reduction of NO_x over Ag/Al_2O_3 and Al_2O_3 catalysts

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Reactivity of surface isocyanate (NCO(a)) species with NO, O_2 and NO + O_2 in selective reduction of NO_x over Ag/Al_2O_3 and Al_2O_3 catalysts was studied by a pulse reaction technique and an *in situ* diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy. The NCO(a) species on Ag/Al_2O_3 reacted with O_2 or NO + O_2 mixture gas to produce N_2 effectively above 200 °C, while the reaction of NCO(a) with NO hardly produced N_2 even at 350 °C. In the case of Al_2O_3 alone, less N_2 was detected in the reaction of NCO(a) with NO + O_2, indicating that silver plays an important role in the N_2 formation from NCO(a). These behaviors of the reactivity of NCO(a) species with reactant gases were in good agreement with the changes in NCO(a) bands shown by *in situ* DRIFT measurements. Based on these findings, the role of NCO(a) species in the selective reduction of NO_x on Ag/Al_2O_3 and Al_2O_3 catalysts is discussed.

Keywords: isocyanate, reactivity, selective reduction of NO_x, Ag/Al_2O_3, Al_2O_3

1. Introduction

Selective catalytic reduction of nitrogen oxides in an oxidizing atmosphere with reductants such as hydrocarbons has attracted much attention since Iwamoto [1] and Held et al. [2] reported on the effectiveness of copper-exchanged ZSM-5 catalyst for this NO_x reduction. Recently, silver catalysts have been investigated as interesting catalysts which perform the relatively high activity for the selective catalytic reduction of NO_x by hydrocarbons (C_3H_6, etc.) or oxygen-containing organic compounds (C_2H_5OH, $(CH_3)_2CO$, etc.) in the presence of excess oxygen [3–12]. In the case of Ag/Al_2O_3, NO_x can be reduced quite effectively with ethanol even in the presence of excess O_2, H_2O and SO_2 [4,6,7].

The adsorbed species on catalysts in the NO_x reduction have been observed by many researchers using infrared spectroscopy, and several intermediates such as isocyanate (–NCO) [13–18], organic nitro (R–NO_2) [19–22], nitrile or cyanide (–CN) [18,23,24], ammonia [25] have been suggested to take part in the selective reduction of NO_x on several catalysts so far. However, a consensus about the intermediates of NO_x reduction has not been obtained yet. Ukisu et al. [13,14] reported a correlation between the efficiency of NO_x reduction with hydrocarbons on copper-containing oxide catalysts and the formation of the NCO species. For Ag/Al_2O_3, we have associated the high efficiency of NO_x reduction by ethanol in the presence of water with the high productivity of a surface isocyanate intermediate even in the presence of water, and suggested that the NCO formation and its reaction with NO in the presence of O_2 are key steps to the efficient NO_x reduction with ethanol [15].

In the past two decades, the behavior of NCO(a) species such as formation, stability and migration had been investigated mainly by IR spectroscopy in the high-temperature reaction between NO and CO on noble metals supported by various oxides [26,27]. Unland [28] studied the reaction of surface isocyanate groups with various reactants such as alcohol and H_2O by observing changes in the IR spectroscopy. He indicated that NCO(a) species was capable of reacting in various ways to produce adsorbed species such as urethane (–NHCOOR) and ammonia (NH_3) [28]. These studies by IR spectroscopy revealed that the formation, stability and reactivity of surface isocyanate species (NCO(a)) strongly depend on the metals and/or supports, as well as the reactants.

The NCO(a) species has been generally regarded as spectator species in the NO + CO reaction to produce N_2 [27]. However, in the recent mechanistic studies of the selective reduction of NO_x with hydrocarbons and alcohol, the NCO(a) species have been discussed as a possible intermediate to produce N_2 [7,13–18,22,29]. A gas-phase product in the reaction of NCO(a) species with NO, O_2 and NO + O_2 has been examined by combining IR spectroscopy with several techniques such as mass spectroscopy and transient response [13,17,22]. In these studies, it should be particularly noted that the reactivity of NCO(a) species has occurred with coexisting reaction gases such as O_2 and NO_2. Nevertheless, little detailed work with respect to the correlation between the reactivity of NCO(a) species and the high catalytic activity in the NO_x reduction on Ag/Al_2O_3 catalyst has been performed. The present work is devoted to an investigation of the specific reactivity of surface isocyanate species (NCO(a)) with NO, O_2 or a NO + O_2 mixture on

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Ag/Al_2O_3 and Al_2O_3 catalysts by using a pulse reaction technique and *in situ* DRIFT (diffuse reflectance infrared Fourier transform) spectroscopy. The role of silver in the surface reaction of NCO(a) to produce N_2 is also examined.

2. Experimental

Ag/Al_2O_3 catalyst (γ-Al_2O_3, 2 wt% Ag) was prepared by an impregnation method described in previous papers [4,5]. The BET surface area of this Al_2O_3 support was 251 m^2/g [5]. All reactant gases were high-purity chemical grade and were used without further purification.

In situ DRIFT measurements were performed by using the same experimental procedures as in a previous paper [30]. Surface isocyanate (NCO(a)) species were prepared on Ag/Al_2O_3 and Al_2O_3 as follows: Ag/Al_2O_3 and Al_2O_3 samples pretreated with O_2 (20% O_2/He, 100 ml/min) at 500 °C for 1 h in a DRIFT cell were exposed to a gas mixture of NO (1000 ppm), ethanol (900 ppm) and O_2 (10%) in He at total flow rate of 50 ml/min (total pressure: 1 atm) at 150 °C for 1 h, followed by heating the sample under He flow up to 350 °C (60 ml/min, 10 °C/min). It should be noted that the reproducibility of the formation of surface NCO(a) species after this treatment had been verified by the DRIFT. This procedure is hereafter referred to as *formation of NCO(a) treatment*. For pulse experiments, the same set of these treatments were performed with Ag/Al_2O_3 and Al_2O_3 samples (50 mg) in a fixed-bed flow reactor before pulse reaction.

Reactivity of the surface isocyanate species on catalysts was measured by a pulse reaction technique. The pulse experiment was carried out at 150–350 °C after the formation of NCO(a) treatment. The products were analyzed by an on-line gas chromatograph (Shimadzu GC-14A) equipped with Molecular Sieve 5A (N_2 and CO) and Porapak Q (N_2O and CO_2) and by a mass spectrometer (SKK Vacuum Eng., Microvision). A pulse of 1 ml was introduced into the reactor, which contained 41 nmol/NO-pulse and/or 4115 nmol/O_2-pulse in He balance (He carrier gas: 50 ml/min; space velocity: 10000 h^{-1}). On the other hand, the reactions of NCO(a) species with NO, O_2 and $NO + O_2$ on Ag/Al_2O_3 and Al_2O_3 catalysts were also monitored by *in situ* DRIFT spectroscopy. In order to unify the total number of moles of NO and/or O_2 flowed with the pulse experiment, the DRIFT experiments were carried out under the following condition: a gas mixture of NO (100 ppm) and/or O_2 (1%) in He at total flow rate of 10 ml/min (total pressure: 1 atm) at 250 °C for 20 min (in 20 min: 8.2×10^{-7} mol NO and/or 8.2×10^{-5} mol O_2).

3. Results and discussion

3.1. In situ DRIFT measurements in formation and reactivity of NCO(a) species

We have already reported that the Ag/Al_2O_3 catalyst in the $NO + O_2 +$ ethanol system showed extremely high NO_x conversion into N_2 at a temperature range 250–400 °C (~86%), while the catalytic activity of Al_2O_3 was lower than that of Ag/Al_2O_3 at temperatures below 400 °C (<45%) [6,31]. This result indicates that the NO_x conversion with ethanol is strongly promoted by the presence of silver. In order to elucidate the differences in NO_x conversion between Ag/Al_2O_3 and Al_2O_3, we have investigated the role of silver as well as the reactivity of surface NCO(a) species on Ag/Al_2O_3 and Al_2O_3 in selective reduction of NO_x. First, the formation and reactivity of NCO(a) species on Ag/Al_2O_3 and Al_2O_3 catalysts were monitored by *in situ* DRIFT spectroscopy.

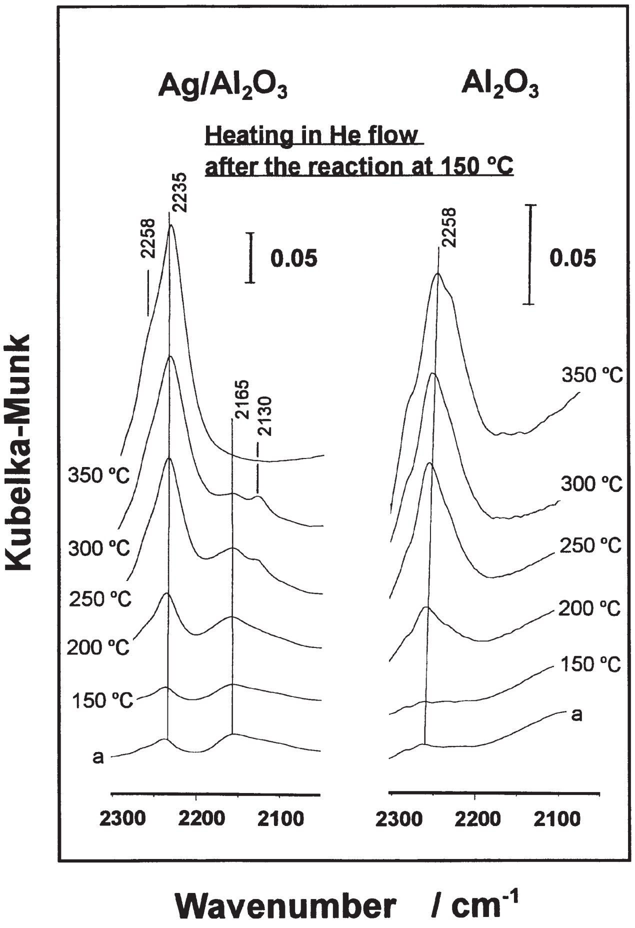

Figure 1. DRIFT spectra of the NCO band during the heating process in He flow on Ag/Al_2O_3 and Al_2O_3 catalysts. (a) After the exposure of NO (1000 ppm)/O_2 (10%)/ethanol (900 ppm) reaction mixture (He balance: 50 ml/min) at 150 °C for 30 min.

Figure 1 shows DRIFT spectra in the 2300–2100 cm^{-1} region of the Ag/Al_2O_3 and Al_2O_3 catalysts at 150 °C in $NO + O_2 +$ ethanol followed by heating in the He flow (60 ml/min) (formation of NCO(a) treatment, see section 2). Two intense bands were observed at 2235 and 2258 cm^{-1} (shoulder) on Ag/Al_2O_3, while an intense band was at 2258 cm^{-1} on Al_2O_3. The IR band in this region can be assigned to an asymmetric stretching band of NCO(a) species on Ag/Al_2O_3 and Al_2O_3 because we observed the band at the same position in the isocyanic acid (HNCO) adsorption on Ag/Al_2O_3 at 250 °C [30]. The intense IR bands

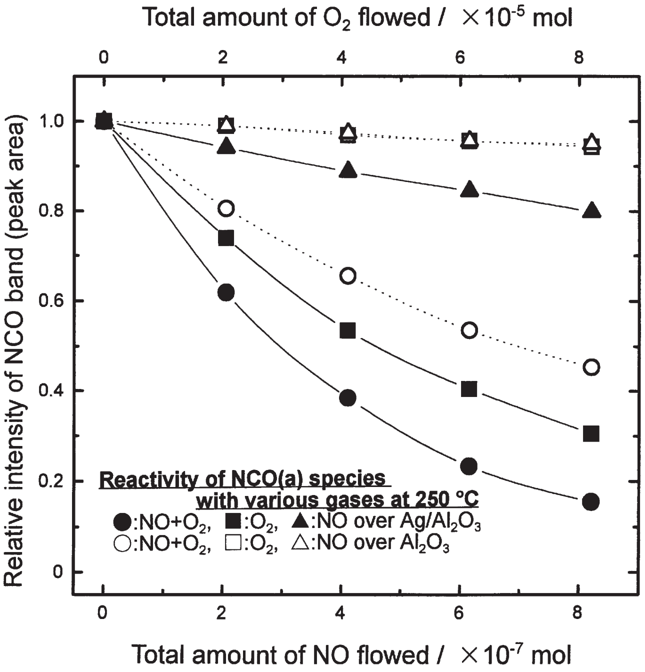

Figure 2. Change in intensity of the NCO band (peak area) on Ag/Al_2O_3 and Al_2O_3 catalysts during the exposure of $NO + O_2$ mixture, NO and O_2 at 250 °C.

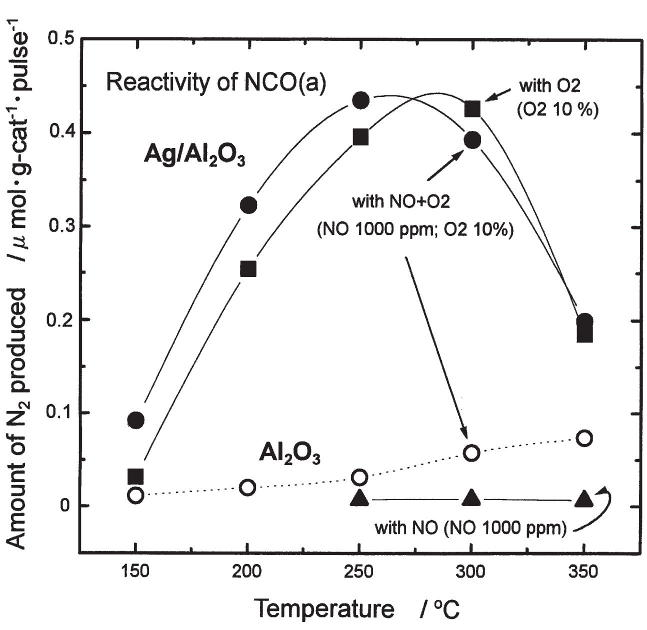

Figure 3. Temperature dependence of N_2 formation by the reaction of NCO(a) species with NO (1000 ppm) + O_2 (10%) mixture, O_2 (10%) and NO (1000 ppm) pulse (1 ml/pulse; He balance; NO: 41 nmol/pulse; O_2: 4115 nmol/pulse) on Ag/Al_2O_3 and Al_2O_3.

at 2235 and 2258 cm^{-1} are assigned to NCO(a) on a silver (Ag–NCO) and Al_2O_3 support (Al–NCO), respectively [15,27]. As shown in figure 1, the formation of NCO(a) species is enhanced by the presence of silver, because the NCO band on Ag/Al_2O_3 is more intense than that on Al_2O_3 under the same treatment conditions. The bands at 2165 and 2130 cm^{-1} may be assigned to a C≡N stretching band of two different CN(a) species on Ag/Al_2O_3 [30], which disappeared at 350 °C in He flow. The intensities of the NCO(a) band on both Ag/Al_2O_3 and Al_2O_3 were increased by heating the sample in He flow (up to 350 °C). It should be noted that the NCO(a) formation occurred even in the absence of silver (Al_2O_3 alone) during the heating in He flow. The thermal stability of NCO(a) species on Ag/Al_2O_3 and Al_2O_3 was very high (figure 1), but disappeared above 500 °C in He flow [30].

Figure 2 shows the change of NCO(a) bands on Ag/Al_2O_3 and Al_2O_3 during the stream under NO, O_2 and NO + O_2 flow. In the case of Ag/Al_2O_3, NCO(a) bands decreased significantly under O_2 or NO + O_2 flow, while little change was observed under NO flow. In the case of Al_2O_3, the decrease of the NCO(a) band under NO + O_2 flow was much faster than that under NO or O_2 flow. These results suggest that NCO(a) reacts with NO + O_2 (presumably NO_2) even in the absence of silver, while the reaction of NCO(a) with O_2 proceeds only in the presence of silver. Products such as N_2 and CO_2 in the reaction of NCO(a) with NO, O_2 and NO + O_2 could not be determined reliably by this DRIFT system because the concentration of products was diluted by He flow. In order to examine the products in these reactions, the products were analyzed by using a pulse reaction technique. We describe the correspondence between the DRIFT data and products in the next section.

3.2. Reaction of NCO(a) species with NO, O_2 and NO + O_2 by pulse reaction

Figure 3 shows the temperature dependence of N_2 formation in the reaction with a pulse of NO + O_2, O_2 or NO over Ag/Al_2O_3 and Al_2O_3 after formation of NCO(a) treatment (see experimental section). By analysis of the gas phase with GC and/or mass spectrometer (MS), other products such as N_2O (except N_2, CO_2 and CO) were hardly detected in all cases. As shown in figure 3, the N_2 formation on Ag/Al_2O_3 depended on the reactant gases. Additionally, the change in the intensities of NCO bands also depended on the reactant gases (figure 2). Therefore, the N_2 formation correlated well with the decreases in the intensities of NCO bands. On the other hand, it was confirmed by the labeled experiments on a static condition that $^{15}N_2$ and $^{14}N^{15}N$ were detected as main products of dinitrogen after the reaction of $^{15}NCO(a) + O_2$ and $^{15}NCO(a) + {}^{14}NO + O_2$ at 250 °C for 0.5 h, respectively [32]. On the basis of the above results, it is concluded that NCO(a) species is involved in the N_2 formation. In the reaction of NCO(a) with NO + O_2 pulse, the Ag/Al_2O_3 catalyst showed high efficiency of N_2 formation at a temperature range between 200 and 300 °C, while the N_2 formation on Al_2O_3 occurred above 250 °C. In the case of Ag/Al_2O_3, N_2 formation by the reaction of NCO(a) with O_2 pulse also occurred above 200 °C, while the N_2 formation by the reaction of NCO(a) with NO pulse was very low even at 350 °C. The results of this pulse reaction prove that silver plays an important role in the reaction of NCO(a) with O_2 to produce N_2, i.e., silver promotes the

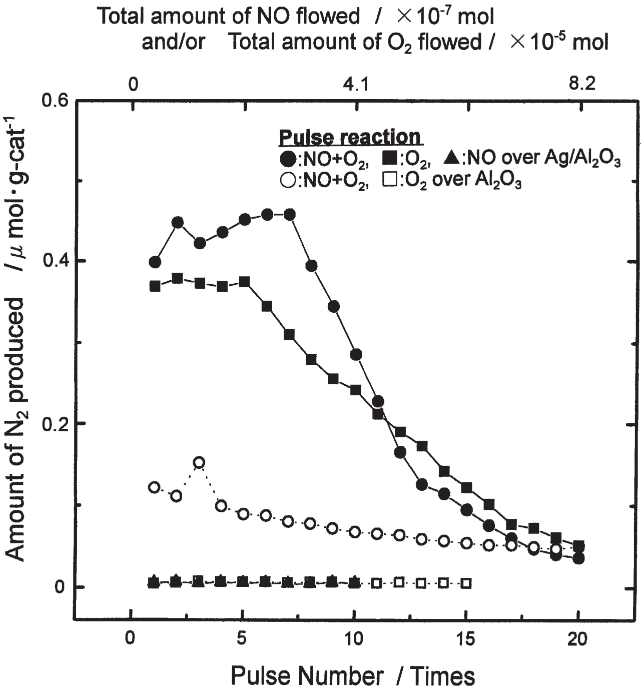

Figure 4. Pulse number dependence of N_2 formation by the reaction of NCO(a) species with NO (1000 ppm) + O_2 (10%) mixture, O_2 (10%) and NO (1000 ppm) pulse (1 ml/pulse; He balance; NO: 41 nmol/pulse; O_2: 4115 nmol/pulse) on Ag/Al_2O_3 (at 250 °C) and Al_2O_3 (at 350 °C).

activation of oxygen and/or the formation of NO_2. In spite of no N_2 formation in the reaction of NCO(a) with NO on Ag/Al_2O_3, the intensity of the NCO(a) band decreased with time under NO flow (figure 2). The NCO(a) species may have converted to other adsorbed species such as CN(a) under NO flow at 250 °C, since an increase of the bands at 2165 and 2130 cm^{-1} was observed (spectra not shown). Temperatures higher than 300 °C led to a decrease in the N_2 formation over Ag/Al_2O_3 (figure 3), probably because O_2 in the pulse was completely consumed by the preferential oxidation of other residual species such as partial oxidized species and/or CH_x(a) (residual O_2 was not detected downstream of the reactor in the pulse reaction at 350 °C).

Figure 4 shows the amount of N_2 produced in the pulse experiment at 250 °C (on Ag/Al_2O_3) and at 350 °C (on Al_2O_3) after formation of NCO(a) treatment. The amount of N_2 produced decreased gradually as the pulse number increased because the NCO(a) species on the catalysts were consumed by the reaction with O_2 or NO + O_2. The total amounts of N_2 produced on Ag/Al_2O_3 and Al_2O_3 by the pulse reaction were as follows (for 20 pulses integral of the data in figure 4): 3.8 μmol/g-cat (with O_2 pulse on Ag/Al_2O_3), 5.1 μmol/g-cat (with NO + O_2 pulse on Ag/Al_2O_3) and 1.4 μmol/g-cat (with NO + O_2 pulse on Al_2O_3). If all NCO(a) species on silver and Al_2O_3 are consumed by the reaction with O_2 (2NCO(a) + O_2 → N_2 + $2CO_2$) and with NO_2 (NCO(a) + NO_2 → N_2 + CO_2 + (O)), respectively, the amount of surface NCO(a) species on silver and Al_2O_3 can be estimated to be 7.6 and 1.4 μmol/g-cat, respectively. Based on the dispersion of silver ($D = 0.362$) on Ag/Al_2O_3 [32] and the amount of Lewis acid sites on the Al_2O_3 surface (251 m^2/g; 4×10^{14} site/cm^2 at 350 °C treatment [33]), ca. 11% of the silver surface and <0.5% of the Lewis acid sites on the Al_2O_3 surface were covered by the chemisorbed isocyanate NCO(a), respectively. This coverage of NCO(a) species on silver and Al_2O_3 may be reasonable because other adsorbed species such as NO_3^-(a) and CO_3^{2-}(a) occupied the surface sites of silver and Al_2O_3 during the experiment [30]. In the case of the reaction of NCO(a) with NO + O_2 over the Ag/Al_2O_3 catalyst, the total amount of N_2 produced almost equals the sum of N_2 produced in the reaction with O_2 on silver and the reaction with NO + O_2 on Al_2O_3. This result apparently suggests that N_2 formation by the reaction of NCO(a) with O_2 and NO + O_2 may occur on silver and Al_2O_3 surfaces, respectively. However, the change rate of the NCO(a) band with NO + O_2 over silver (Ag/Al_2O_3) was more rapid than that of the NCO(a) band with NO + O_2 over Al_2O_3 (figure 2). Thus, the reactivity of NCO(a) on silver with NO + O_2 may be higher than that on Al_2O_3. The difference of NO_x reduction activity between Ag/Al_2O_3 and Al_2O_3 would mainly derive from the reactivity of NCO(a) over the silver surface. On the other hand, migration and/or spillover of isocyanate species from metals such as Pt and Rh to oxide supports (e.g., Al_2O_3 and SiO_2) have been reported by several researchers [26,34–36]. During the NO_x reduction in flow condition, migration of NCO(a) species from silver to Al_2O_3 and vice versa on Ag/Al_2O_3 may readily occur depending on the temperature, because the formation, accumulation and reaction of NCO(a) species continue on the silver and/or Al_2O_3 surface.

Recently, Okuhara et al. reported that organic nitro and isocyanate species in the selective reduction of NO_x were highly reactive toward NO_2 and O_2 to form N_2 and N_2O, which was observed over Pt/SiO_2 by *in situ* IR studies and transient response analysis [22]. As reported previously [13,17], NCO(a) on alumina-supported metal catalysts such as Cu/Al_2O_3 reacted with NO as well as O_2 and/or NO + O_2 below 350 °C to produce N_2, CO_2 and CO. In the present work, no N_2O formation and no reaction of NCO(a) with NO were observed over Ag/Al_2O_3 and Al_2O_3. This difference of products and reactivity among supported metals may be derived from mainly the property of supported metals (i.e., the dissociation and/or adsorption of NO occurs readily on platinum and copper surfaces [37,38], while almost no dissociation and/or adsorption of NO occurs on a silver surface). Thus, silver could adequately enhance the activation of O_2 (and NO_2 formation) followed by the reaction of NCO(a) with O_2 or NO_2.

We propose the involvement of NCO(a) species in the N_2 formation on the selective reduction of NO_x (via reactions (1)–(3)):

$$\mathrm{NCO(a)} + \mathrm{NO_2} \rightarrow \mathrm{N_2} + \mathrm{CO_2} + (1/2)\mathrm{O_2}\ (\text{or } \mathrm{O(a)}) \quad (1)$$

$$(\mathrm{NO} + (1/2)\mathrm{O_2}\ (\text{or } \mathrm{O(a)}) \rightleftharpoons \mathrm{NO_2})$$

$$2\mathrm{NCO(a)} + \mathrm{O_2} \rightarrow \mathrm{N_2} + 2\mathrm{CO_2} \quad (2)$$

$$\mathrm{NCO(a)} + \mathrm{NO} \rightarrow \mathrm{N_2} + \mathrm{CO_2} \quad (3)$$

Equations (1) and (2) indicate the reaction of NCO(a) with O_2 and NO_2 to form N_2 (simply showing the overall stoichiometry), but the detailed mechanism is not known at the present stage. Equation (3) hardly took place over Ag/Al_2O_3 and Al_2O_3 catalysts.

4. Conclusion

The present study revealed the correlation between the reactivity of NCO(a) species and the formation of N_2 over Ag/Al_2O_3 and Al_2O_3 catalysts. The NCO(a) species reacted with $NO + O_2$ to produce N_2 on both Ag/Al_2O_3 and Al_2O_3, while the reaction of NCO(a) with O_2 to produce N_2 occurred only in the presence of silver. No N_2 formation was observed by the reaction of NCO(a) with NO over either Ag/Al_2O_3 or Al_2O_3. Thus, silver could adequately promote the activation of O_2 and/or the formation of NO_2 followed by the reaction of NCO(a) with O_2 or NO_2. It is also suggested that the NCO(a) species is the important intermediate in the N_2 formation.

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