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Activity enhancement of copper-containing oxide catalysts by addition of cesium in the reduction of nitric oxide

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Catalytic reduction of nitric oxide in the presence of propylene and oxygen over alumina and copper-containing oxide catalysts has been studied. The optimum temperature for this reaction is dependent upon the composition of the catalysts: ≈ 640 K on Cu–Cs/Al_2O_3, ≈ 680 K on Cu/Al_2O_3, and ≈ 780 K on Al_2O_3. IR spectroscopic measurements show that an isocyanate (–NCO) intermediate formed on Cu–Cs/Al_2O_3 is more reactive with NO to give N_2 than the intermediate produced on Al_2O_3 and Cu/Al_2O_3. Electron donation from Cs to Cu may activate the intermediate.

Keywords: Nitric oxide; catalytic reduction; propylene; copper; cesium; alumina

1. Introduction

Reduction of nitrogen oxides (NO_x) has been an urgent problem to solve for protecting the global environment from air pollution. Emission of NO_x mainly arises from industrial facilities (boilers and power stations, etc.) and automobile engines. Catalytic reduction of NO_x using ammonia as a reducing reagent has already been adopted for industrial stationary sources. For automobile exhaust, a three-way catalyst system is now used to remove NO_x from gasoline engine exhaust. However, catalytic reduction of NO_x from diesel engine exhaust is not developed yet, because the usual catalysts are poisoned by the high concentration of oxygen contained in the exhaust [1].

In recent years, catalytic reduction of NO_x with hydrocarbons as reducing reagents in the presence of oxygen, $NO + \text{hydrocarbons} + O_2 \rightarrow N_2 + CO_2 +$

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H_2O, has been investigated intensively using solid catalysts such as alumina [2], cation-exchanged zeolites [3–5], and metal-supported catalysts [6–9]. Catalytic features of these catalysts are significantly dependent upon the composition of the catalysts. For development of high-efficiency catalysts, understanding of molecular aspects of the catalyst surfaces is helpful. We have investigated adsorbed species on Cu-containing alumina-supported catalysts in a $NO/O_2/$propylene system and reported that a surface isocyanate species (–NCO) is a reaction intermediate for the NO_x reduction [10].

In this paper, we describe the catalytic reduction of NO in the presence of O_2 and C_3H_6 over alumina and alumina-supported catalysts containing Cu or Cu and Cs, and discuss the difference in catalytic activity among them in terms of the reactivities of the intermediate species as observed by infrared spectroscopy.

2. Experimental

Catalysts used in this work were an alumina-supported Cu–Cs oxide catalyst (denoted as $Cu–Cs/Al_2O_3$) and a Cu oxide catalyst (Cu/Al_2O_3) as described in a previous paper [10]. $Cu–Cs/Al_2O_3$ contains 1.4 wt% of copper and 2.0 wt% of cesium, and Cu/Al_2O_3 1.3 wt% of Cu. The BET surface area of Al_2O_3 was $\approx 200\ m^2\ g^{-1}$, and no appreciable change was observed after loading of Cu or Cu and Cs onto it.

The catalytic reduction of nitric oxide was carried out in a fixed-bed flow reactor by passing a gas mixture of 800 ppm NO, 10% O_2 and 800 ppm C_3H_6 in helium at a rate of 1200 $cm^3\ min^{-1}$ over 3.0 g of catalyst. The effluent gas was analysed by gas chromatography. The catalytic activity for NO reduction was evaluated by the percentage conversion of NO to N_2.

Infrared spectra were obtained using an Hitachi 270-30 spectrometer. An IR cell made of pyrex glass was used, which has a sample holder, electronic heater and BaF_2 windows. The sample holder is movable from the heater section to the window section in the IR cell. The IR sample was prepared by pressing the catalyst powder, ground in an agate mortar, into a wafer of $\approx 20\ mg\ cm^{-2}$ which was then outgassed at 673 K for 1 h before exposure to the reactant gases. Measurements of IR spectra were all carried out at room temperature. The base pressure of the vacuum line connecting to the IR cell was less than 10^{-6} Torr.

3. Results and discussion

Fig. 1 shows the temperature dependence of the catalytic activity of NO reduction over $Cu–Cs/Al_2O_3$, Cu/Al_2O_3 and Al_2O_3. Catalytic reduction of NO by C_3H_6 occurs in a certain temperature region, since concomitant oxidation of C_3H_6 by O_2 occurs preferentially at higher temperatures. The tempera-

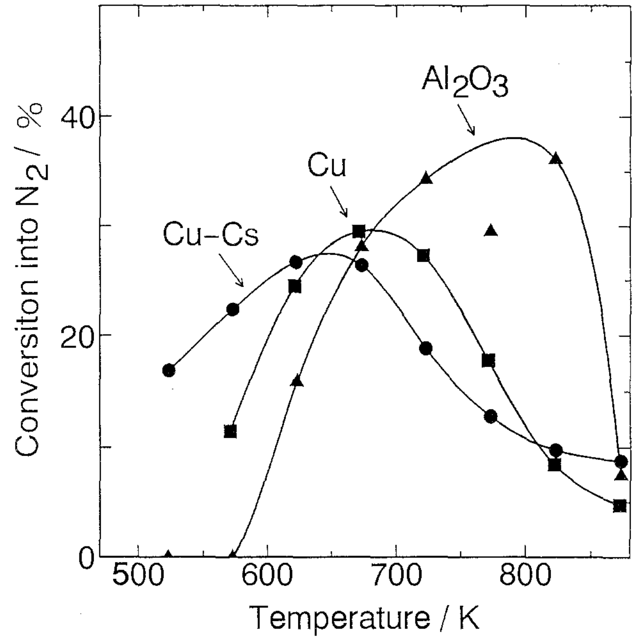

Fig. 1. Temperature dependence of the catalytic activities of alumina and alumina-supported catalysts. Catalyst weight: 3.0 g. NO (800 ppm), C_3H_6 (800 ppm), and O_2 (10%). Gas flow rate: 1200 cm^3 min^{-1}. (●) $Cu-Cs/Al_2O_3$; (■) Cu/Al_2O_3; (▲) Al_2O_3.

ture giving a maximum conversion is dependent upon the composition of the catalysts: ≈ 640 K on $Cu-Cs/Al_2O_3$, ≈ 680 K on Cu/Al_2O_3, and ≈ 780 K on Al_2O_3. It is noteworthy that loading of copper on alumina leads to a significant improvement in catalytic activity at temperatures lower than 670 K, and addition of cesium to the Cu catalyst results in a further increment of activity at temperatures below 620 K. This enhancement of activity at low temperatures has been investigated using IR spectroscopy.

We have found that an isocyanate intermediate was formed during the NO_x reduction using an IR spectroscopic technique [10]. In this experiment, we have observed the behavior of the isocyanate species on Al_2O_3, Cu/Al_2O_3 and $Cu-Cs/Al_2O_3$ to examine its role in low-temperature NO_x reduction. The isocyanate species was prepared by exposing the catalysts to a gas mixture of NO (16 Torr), O_2 (15 Torr) and propylene (4 Torr) at room temperature and then evacuating the gas phase followed by heating to 573 K as described in the previous paper [10].

Fig. 2 shows IR spectra of the isocyanate adsorbate thus produced; its IR absorption bands typically appear at 2230–2270 cm^{-1} and the features of the bands depend on the composition of the catalysts. On the alumina catalyst, the band is observed at 2262 cm^{-1} with a shoulder at 2236 cm^{-1}. The isocyanate band on the Cu/Al_2O_3 catalyst splits into two distinct bands, 2266 and 2230

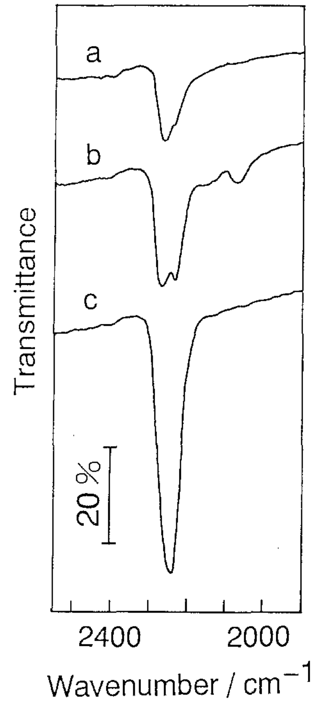

Fig. 2. IR spectra of the isocyanate species formed on the alumina and alumina-supported catalysts: (a) Al_2O_3, (b) Cu/Al_2O_3, (c) $Cu-Cs/Al_2O_3$.

cm^{-1}. These results indicate that two kinds of adsorbed species are formed on the Al_2O_3 and Cu/Al_2O_3 catalysts. It is known that the IR absorption band of the cyanate anion NCO^- is observed at lower frequency; HNCO (NCO covalently bound to the H atom) and K^+NCO^- (NCO^- ionically bound to K^+) provide IR bands at 2246 [11] and 2163 cm^{-1} [12], respectively. On noble metal catalysts, two IR bands are observed at 2270–2150 cm^{-1} in the reaction of NO with CO; the band at higher frequencies is assigned to covalently bound -NCO and the band at lower frequencies to NCO^- [13,14]. This assignment is applicable to the isocyanate bands observed in the present system, although the frequencies of the bands slightly change depending on the composition of the catalysts. Other weak bands observed at around 2150 and 2080 cm^{-1} on the Cu/Al_2O_3 catalyst are tentatively assigned to cyanide (-CN) and isocyanide (-NC), respectively [15]. Fig. 2 also shows that the isocyanate band observed on $Cu-Cs/Al_2O_3$ is much more intense and shifted to lower frequency than the one observed on the other catalysts. Because the IR band of adsorbed species usually shifts to lower frequencies by negatively charging up [13,14], this shift of the isocyanate band may arise from electron transfer from the catalyst to the isocyanate species.

The reaction of the isocyanate species with NO, which leads to the formation of N_2 through the reaction of $-NCO + NO \rightarrow N_2 + CO_2$, is a key step in the

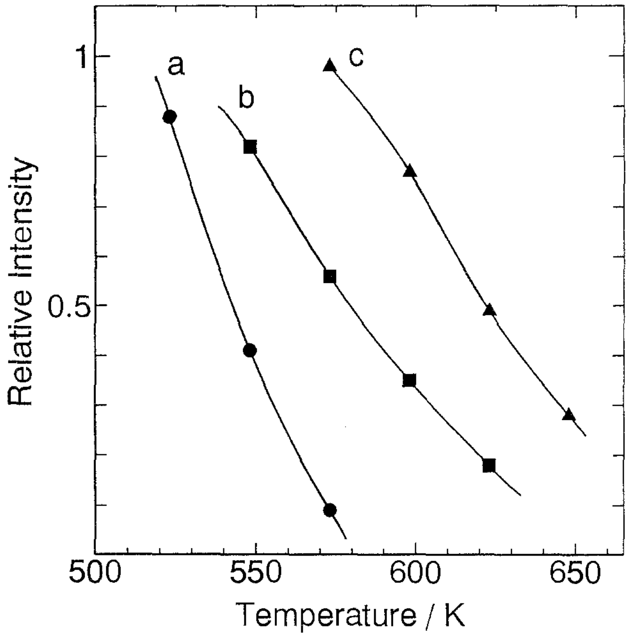

Fig. 3. Temperature dependence of the intensity of the isocyanate band in the presence of NO. (a) $Cu-Cs/Al_2O_3$, (b) Cu/Al_2O_3, (c) Al_2O_3. The band intensity was normalized with respect to the intensity observed before exposure to NO.

NO_x reduction [10,14]. Fig. 3 presents the spectral intensity of the isocyanate band in the presence of NO (15 Torr) as a function of catalyst temperature. The temperature was raised at intervals of 25 K and kept at each temperature for 15 min. On $Cu-Cs/Al_2O_3$, the isocyanate readily reacts with NO at lower temperatures, although a higher temperature is required for this reaction on Cu/Al_2O_3 and Al_2O_3. This result explains well the observed activity order of the catalysts for the low-temperature NO_x reduction, provided that the reaction of the isocyanate species with NO is the rate-determining step of the NO_x reduction.

There are two important factors for the efficient reaction between isocyanate and NO. One is the catalytic activation of isocyanate species, and the other the spontaneous adsorption of NO on catalysts. We have found that NO is adsorbed on Cu/Al_2O_3 and $Cu-Cs/Al_2O_3$ but not on Al_2O_3. Therefore, the low catalytic activity of Al_2O_3 may be due to the poor adsorption of NO on Al_2O_3. As shown in fig. 2, the adsorption state of isocyanate species on $Cu-Cs/Al_2O_3$ is different from that on Cu/Al_2O_3 and Al_2O_3, while the adsorption state of NO and its adsorption amount on the Cu/Al_2O_3 and the $Cu-Cs/Al_2O_3$ catalysts are virtually the same. This leads us to conclude that the high catalytic activity of $Cu-Cs/Al_2O_3$ as compared to Cu/Al_2O_3 is ascribable to the activation of isocyanate species by the electron donation of Cs to Cu.

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