Surface isocyanate intermediate formed during the catalytic reduction of nitrogen oxide in the presence of oxygen and propylene

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IR spectroscopic measurements have revealed that an IR band ascribable to adsorbed isocyanate species grows up when alumina-supported Cu-Cs oxide catalyst is exposed to a mixture of NO, O_2 and C_3H_6 at room temperature and subsequently heated to 400°C in vacuum. The species produces N_2, CO_2 and CO in the ratio of ca. 2:1:1 in the presence of NO at 350°C. Alumina and alumina-supported Cu oxide catalyst are less active for the formation of isocyanate species.

Keywords: Nitrogen oxides reduction; propylene; copper; cesium; alumina

1. Introduction

The development of new catalysts for reduction of NO_x from automobile exhaust, especially from the exhaust of diesel engines, is a current problem in protecting ourselves from global air pollution. Difficulty in the NO_x reduction arises from the high concentration of oxygen in the exhaust gases because the usual three-way catalyst system for automobiles cannot be used in oxygen-rich conditions [1]. A selective catalytic reduction process using ammonia as a reducing reagent is now widely used to remove NO_x from stationary sources in oxygen-rich atomospheres, but this process is unsuitable for small scale oxygen-rich NO_x emissions such as the exhaust of diesel engines. Recently, it has been reported that NO is reduced to N_2 with hydrocarbons as reducing reagents even in the presence of excess O_2 using solid catalysts such as Cu containing catalysts [2,3], alumina [4], zeolites [5] and Cu-zeolites [6–8]. Since the exhaust of diesel engines involves some hydrocarbons such as ethylene, propane and propylene,

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this process is hopeful for practical NO_x-reduction. However, little information has been obtained about the reaction mechanism or reaction intermediates. In this paper we report adsorbed species in the NO-O_2-C_3H_6 system on alumina-supported Cu-Cs oxide catalyst which shows a high activity for the No_x reduction [9] and discuss an intermediate species of the NO reduction.

2. Experimental

Al_2O_3 was obtained from Asahikasei. Catalyst containing Cu and Cs was prepared by impregnating alumina with aqueous solutions of $CuCl_2$ and $CsNO_3$, drying at 40°C, and calcining in air at 700°C for 3 h (denoted as Cu-Cs/Al_2O_3). The concentrations of copper and cesium in the catalyst were determined by atomic absorption analysis to be 1.4 and 2.0 wt%, respectively. Alumina-supported Cu oxide catalyst, containing 1.3 wt% Cu, was prepared in the same manner. For IR measurements, the catalyst was ground in an agate mortar, pressed into a wafer of ca. 20 mg cm^{-2} and subsequently outgassed at 400°C for 1 h in a Pyrex IR cell with BaF_2 windows before exposure to reactant gases. Measurements of IR spectra were all carried out at room temperature. Reactions between surface adsorbed species and gases were done with 0.3 g of catalyst in a closed vessel (34 cm^3). Gases evolved during the reactions were analysed by mass spectroscopy. Mass analyses of mixtures of N_2 and CO or N_2O and CO_2 were carried out using ^{15}NO as a reactant to distinguish N_2 from CO and N_2O from CO_2.

3. Results and discussion

When Cu-Cs/Al_2O_3 is exposed to 16.1 Torr of NO at room temperature, a band at 1882 cm^{-1} appears (spectrum b in fig. 1). This band is attributable to physisorbed NO on the surface, since it disappears readily upon brief pumping at room temperature. The addition of oxygen (13.9 Torr) leads to a drastic change in the spectrum: the NO band shifts slightly to 1896 cm^{-1} with a decrease in intensity, and several new bands grow up at 2220, 1748, 1590 and 1280 cm^{-1} (spectrum c). London et al. [10,11] have reported the IR spectra of NO_2 and N_2O adsorbed on copper oxide and assigned 1740 cm^{-1} band to adsorbed N_2O_4, 1575 and 1265 cm^{-1} to bidentate NO_3^-, 1520 cm^{-1} to monodentate NO_3^-, and 2220 cm^{-1} to adsorbed N_2O. Their assignment of the bands explains well spectrum c. The NO_3^- bands are stable even at 300°C under vacuum, although the N_2O and N_2O_4 bands readily disappear upon brief pumping at room temperature. Subsequent addition of C_3H_6 (3.2 Torr) results in broad bands at around 1660 and 1500 cm^{-1} (spectrum d), and a large amount of CO is detected in the gas phase by mass spectroscopy. Since nitrogen oxides,

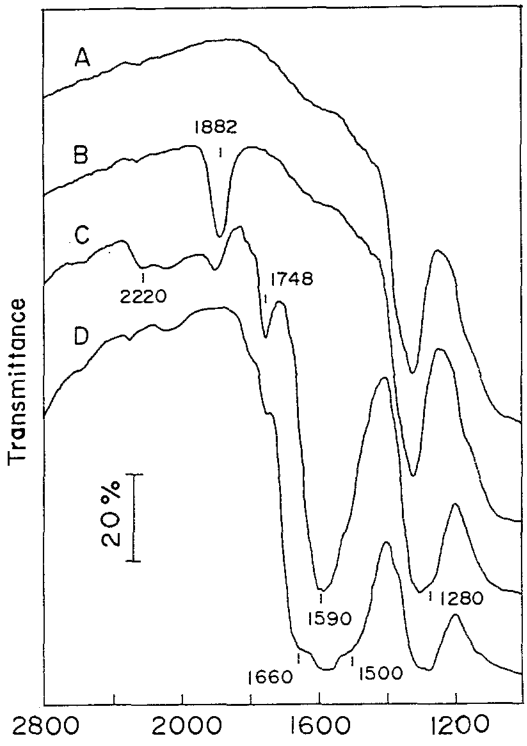

Fig. 1. Infrared spectra of adsorbed species on Cu-Cs/Al_2O_3; (A) background, (B) NO (16.1 Torr), (C) addition of O_2 (13.9 Torr) to (B), (D) addition of C_3H_6 (3.2 Torr) to (C).

especially N_2O_4, are known to be strong oxidizing reagents [12], propylene could be oxidized to CO and other products. We tentatively assign the band at around 1660 cm^{-1} to C=N structure [13] of $NO_x \cdot C_yH_z$ complexes formed in the reaction of NO_x with propylene. The 1500 cm^{-1} band can be assigned to monodentate NO_3^- species.

It is noteworthy that a new band appears at 2240 cm^{-1} when the sample is heated under vacuum at 200°C (spectrum a in fig. 2). With a further rise in heating temperature up to 300°C the band slightly shifts to 2234 cm^{-1} and increases in intensity with a concomitant decrease of the bands at around 1600 and 1300 cm^{-1} (spectrum b). The adsorbed species giving the band at 2234 cm^{-1} is stable even at 400°C under vacuum (spectrum c). It has been reported that M-NCO (adsorbed isocyanate) band is observed in the 2180–2270 cm^{-1} region during the reaction of NO with CO on Cu/SiO_2 [11] and noble metal catalysts [13–16]. It is therefore most likely that the band at 2234 cm^{-1} is assigned to a surface isocyanate species, which may arise from the thermal decomposition of a precursor complex, $NO_x \cdot C_yH_z$.

When the surface –NCO species is exposed to 15.8 Torr of NO at 350°C for 30 min, the 2234 cm^{-1} band completely disappears. Mass spectrometric analysis

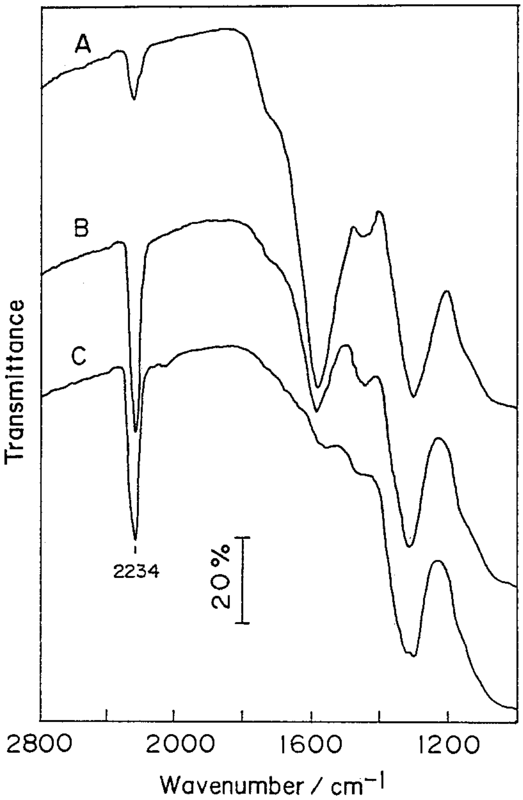

Fig. 2. Change in infrared spectrum of adsorbed species in spectrum d of fig.1 by evacuation of the gas phase for 15 min: Temperature; (A) 200°C, (B) 300°C, (C) 400°C.

of the gas phase showed the formation of N_2, CO_2 and CO in the ratio of ca. 2:1:1. Exposure to O_2 at 350°C also results in elimination of the 2234 cm^{-1} band from the spectrum, and in this case CO_2 is a main product with a small amount of N_2. No N_2 is formed upon exposure to C_3H_6 at 350°C.

We have found that Al_2O_3 and Cu/Al_2O_3 which are less active for the NO_x reduction than Cu-Cs/Al_2O_3 [9]. On such inactive catalysts, the isocyanate band is also observable under a similar condition but the band intensity on Cu/Al_2O_3 and Al_2O_3 is ca. 40% and ca. 30% of the one on Cu-Cs/Al_2O_3, respectively, and temperature above 400°C is required to eliminate the isocyanate band in the presence of NO. This result suggests that the formation of the isocyanate intermediate and/or its reaction with NO at lower temperature are a key to efficient NO reduction in the presence of O_2.

In conclusion, a surface isocyanate species is found to be a reaction intermediate in the N_2 formation in the NO + O_2 + C_3H_6 system, and Cu-Cs/Al_2O_3 is so active for the isocyanate formation as to be a strong candidate for a practical NO_x-reduction catalyst for automobile exhaust. Infrared study on the NO_x

reduction system including other hydrocarbons such as ethylene and propane is under progress in our laboratory.

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