Catalysis Letters 39 (1996) 265–267

Infrared study of catalytic reduction of lean NOx with alcohols over alumina-supported silver catalyst

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Received 27 October 1995; accepted 4 March 1996

Two intense IR absorption bands due to surface isocyanate (–NCO) species have been observed at 2262 and 2232 cm^{-1} when an alumina-supported silver catalyst is exposed to a mixture of NO, O_2 and ethanol at 150°C and subsequently heated to $> 300°C$ in vacuum. The intensity of the isocyanate band is hardly affected by the water existing in the mixture. Methanol is less reactive than ethanol for the formation of isocyanate species. The reaction mechanism of catalytic reduction of lean NOx with alcohols is discussed based on these IR spectroscopic findings.

Keywords: lean NOx; catalytic reduction; ethanol; methanol; silver; alumina

1. Introduction

There has been a considerable progress in catalytic reduction of nitrogen oxides from diesel engine exhaust and other oxygen rich fuel gases (lean NOx) [1]. A number of solid catalyst systems have been investigated including the utilization of various hydrocarbons as reductants. For practical use, recent research on the reduction of lean NOx has been focused on the resolution of catalyst poisoning due to the presence of water. Miyadera et al. reported that oxygen-containing organic compounds such as ethanol and acetone are extremely effective in reducing lean NOx over Ag/Al_2O_3 even in the presence of water [2,3], while water interferes with the reaction using propylene as the reductant [4,5].

There has been little information on the mechanism and the reaction intermediates of lean NOx catalysis with some hydrocarbon reductants. In this study, an isocyanate species (–NCO) was observed on copper-containing oxide catalysts in a NO/O_2/propylene system, and it is suggested that the isocyanate species is a strong candidate for the intermediate of lean NOx reduction because a satisfactory amount of N_2 can be obtained from the reaction between adsorbed NCO and NO [6,7]. In the recent infrared studies on lean NOx reduction, several surface species such as isocyanate species [9–12], $-(N_xO_y)_z$ species [9], –CN species [11–13] and nitro compounds [10] have been observed on several catalysts. However, these species were observed under conditions where no water is present. In the author's previous study, it has been reported that water adsorbed on the catalyst surface suppresses the formation of isocyanate species in NO/O_2/hydrocarbons systems [8].

This paper reports the observation of species adsorbed on the surface of an alumina-supported silver catalyst in a NO/O_2/ethanol (or methanol) system both in the absence and in the presence of water, and discusses the intermediate species in lean NOx reduction.

2. Experimental

The catalyst used in this work was an alumina-supported silver catalyst (denoted as Ag/Al_2O_3) prepared by an impregnation method described in a previous paper [2]. The concentration of silver was 4.6 wt%. All gases used were of industrial high-purity grade without further purification. Ethanol, methanol and water were purified by freeze–pump–thaw techniques.

FT-IR spectra were obtained using a Nicolet Magna 550 spectrometer with a resolution of 2 cm^{-1} and an average of 50 scans. An IR cell made of Pyrex glass was used, containing a sample holder, electronic heater and NaCl windows. The sample holder can be moved from the heater section to the window section in the IR cell. The IR sample was prepared by pressing catalyst powder ground in an agate mortar into a wafer of ca. 20 mg cm^{-2}. A dehydrated sample was prepared in the IR cell by outgassing a fresh sample at 300°C for 30 min and then oxidizing under ca. 50 Torr of O_2 at 300°C for 30 min followed by briefly pumping at room temperature. All IR measurements were carried out at room tempera-

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ture. The base pressure of the vacuum line connecting to the IR cell was kept lower than 10^{-5} Torr (1 Torr = 133.3 Pa).

3. Results and discussion

3.1. $NO + O_2 + C_2H_5OH$

The dehydrated Ag/Al_2O_3 sample was exposed to a gas mixture of NO (14 Torr), O_2 (15 Torr) and C_2H_5OH (11 Torr) at 150°C for 15 min and then heated stepwise in vacuum for 15 min. Fig. 1A shows the IR spectral change of the adsorbed species with increasing heating temperature in vacuum. In the 1600–1300 cm^{-1} region, very intense bands due to NO_3^- species were observed, even after the temperature was raised to 350°C (this region is not shown in the figure). When the heating temperature was elevated to $> 300°C$, two intense bands appeared at 2262 and 2232 cm^{-1}, which are attributable to adsorbed isocyanate species (–NCO) as observed in other NO/O_2/hydrocarbons systems [6–12]. It is known that isocyanato complexes have two IR active modes, giving an antisymmetric stretching band of NCO at around 2200 cm^{-1} and a symmmetric stretching band of NCO at around 1300 cm^{-1} [14]. In our system, however, the symmetric stretching band cannot be observed because of overlapping of the intense bands caused by NO_3^- species. The 2262 and 2232 cm^{-1} bands can be attributed to NCO on Al_2O_3 and Ag–NCO, respectively, because only a band of higher frequency was observed on Al_2O_3 in the same situation (see fig. 1A(f), dotted line). Preheating of the catalyst in the gas mixture at 150°C before heating in vacuum is required for the appearance of intense isocyanate bands, probably because it enables the production of a precursor compound of isocyanate postulated for the NO/O_2/hydrocarbons system [6]. The isocyanate band readily disappeared upon exposure to NO at 250°C. This suggests the isocyanate species to be an intermediate species of NOx reduction, since adsorbed NCO produces N_2, CO_2 and CO in the presence of NO as described in previous papers [6,7]. In the 3000–2850 cm^{-1} region, weak bands attributable to C–H stretching were observed even at higher temperatures, indicating that small amounts of CH_x residues have been adsorbed on the catalyst surface.

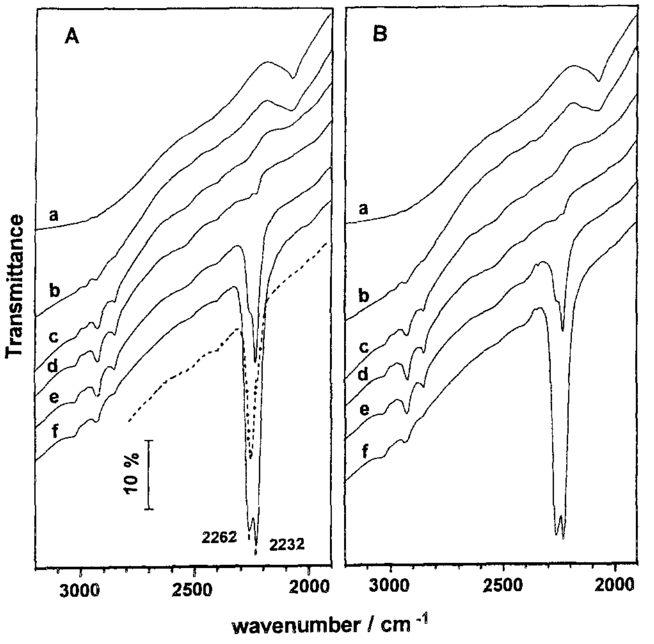

Fig. 1. FT-IR spectra of adsorbed species formed on dehydrated Ag/Al_2O_3 (solid line) and Al_2O_3 (dotted line) after exposure to (A) a mixture of NO (14 Torr) / O_2 (15 Torr) / C_2H_5OH (11 Torr) and (B) a mixture of NO (14 Torr) / O_2 (15 Torr) / C_2H_5OH (11 Torr) / H_2O (2 Torr) at 150°C for 15 min and subsequent heating in vacuum for 15 min: temperature (a) room temperature, (b) 100°C, (c) 200°C, (d) 250°C, (e) 300°C, (f) 350°C.

To demonstrate the influence of water, the same procedure was done for IR spectroscopic measurements with a gas mixture of $NO + O_2 + C_2H_5OH$ including H_2O (2 Torr). The spectral change is shown in fig. 1B. It should be noted that the intensity of the isocyanate band was hardly affected by the presence of water. This new finding is quite unlike hydrocarbons (propylene, acetylene or *n*-heptane) containing systems where the formation of isocyanate is considerably supressed by water adsorbed on the catalyst [8]. It has been shown that ethanol is extremely effective for catalytic reduction of lean NOx even in the presence of water; the conversion of NOx was > 80% at temperatures 250–400°C in the presence of 10% water [2,3]. Therefore, the high productivity of isocyanate intermediate in the ethanol containing system with the presence of water promotes efficient NOx reduction in the presence of water.

In catalytic reduction of lean NOx with ethanol, especially with the presence of water, a substantial amount of nitrogen containing by-products such as NH_3, CH_3CN and HCN was obtained with N_2 [15]. It is assumed that ammonia is produced by the following reactions between isocyanate species and water as suggested by London [16]:

$$-NCO + H_2O \rightarrow -OH + HNCO \qquad (1)$$

$$HNCO + H_2O \rightarrow H_2NCOOH \rightarrow NH_3 + CO_2 \qquad (2)$$

Furthermore, it is believed that surface isocyanate reacts with alcohols to form a surface urethane (–NHCOOR) [17]. Thus, surface isocyanate is capable of reacting in various ways to produce adsorbed nitrogen containing species, which may undergo subsequent reactions with ambient gases to form undesirable by-products, although the reaction mechanism is not clear at present.

3.2. $NO+O_2+CH_3OH$

IR spectroscopic measurements were also done in the NO/O_2/CH_3OH system. Methanol is less reactive in

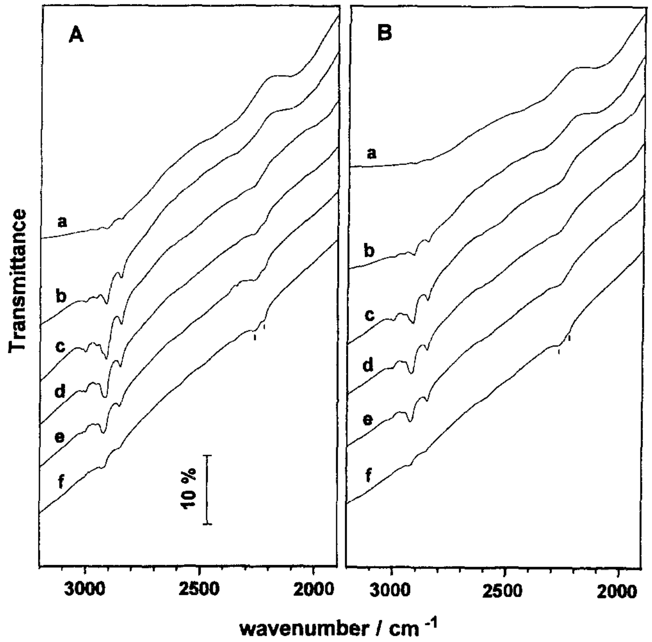

Fig. 2. FT-IR spectra of adsorbed species formed on dehydrated Ag/ Al_2O_3 after exposure to (A) a mixture of NO (14 Torr) / O_2 (15 Torr) / CH_3OH (11 Torr) and (B) a mixture of NO (14 Torr) / O_2 (15 Torr) / CH_3OH (11 Torr) / H_2O (2 Torr) at 150°C for 15 min and subsequent heating in vacuum for 15 min: temperature (a) room temperature, (b) 100°C, (c) 200°C, (d) 250°C, (e) 300°C, (f) 350°C.

reducing lean NOx on Ag/Al_2O_3; the conversion of NOx was less than 5% at temperatures above 250°C in the presence of 10% H_2O [2]. The experimental conditions and procedures for isocyanate formation were the same as for the C_2H_5OH-containing system. Figs. 2A and 2B show the IR spectra of adsorbed species formed in the $NO/O_2/CH_3OH$ system with and without water, respectively. Unlike the C_2H_5OH-containing system, very weak bands due to surface isocyanate were observed after evacuated at > 300°C. This strongly suggests again that isocyanate species is a reaction intermediate of catalytic reduction of lean NOx with alcohols. Such significant difference between CH_3OH and C_2H_5OH for isocyanate formation is an important problem to be resolved in future.

4. Conclusion

IR spectroscopic measurements revealed that high efficiency of lean NOx reduction with ethanol in the presence of water is due to the high productivity of surface isocyanate intermediate in the water containing system. Lower reactivity of methanol in isocyanate formation may lead to low efficiency of lean NOx reduction with methanol.

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