Catalysis Letters 51 (1998) 11–14

Role of organic nitro compounds in selective reduction of NO_x with ethanol over different supported silver catalysts

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Received 13 November 1997; accepted 29 January 1998

The adsorption of organic nitro compounds such as nitromethane and nitroethane on different supported silver catalysts (Ag/Al_2O_3, Ag/TiO_2, Ag/SiO_2) has been studied using infrared spectroscopy. The adsorbed NCO species formation was strongly influenced by the catalyst support and therefore clearly detected on Ag/Al_2O_3 and Ag/TiO_2 catalysts by thermal decomposition of nitromethane and nitroethane at temperatures higher than 150 °C. With the Ag/SiO_2 catalyst, very little NCO formation was observed at 350 °C. On the other hand, the catalyst support was found to affect the N_2 formation in the selective reduction of NO_x on supported silver catalysts. On the basis of these findings, the role of adsorbed nitromethane, nitroethane and isocyanate species in the selective reduction of NO_x is discussed with respect to the catalyst support effect and the catalytic activity.

Keywords: selective reduction of NO_x, supported silver catalyst, support effect, nitromethane, nitroethane

1. Introduction

The catalytic reduction of nitrogen oxides (NO_x) by hydrocarbons (C_3H_6, C_2H_4, etc.) or oxygen-containing organic compounds (C_2H_5OH, $(CH_3)_2CO$, etc.) has recently attracted much attention as a new deNO_x process for diesel and lean-burn gasoline engine exhaust [1,2]. Catalysts such as Cu-exchanged ZSM-5 [1] and alumina-supported metals [2] have been reported to be quite effective in NO_x reduction. Nevertheless, most of these catalysts have been found to be less active in the presence of water vapor. Recent experiments in our laboratory have revealed that NO_x can be reduced quite effectively with oxygen-containing organic compounds such as ethanol and acetone over an alumina-supported silver catalyst (Ag/Al_2O_3) even in the presence of excess oxygen and water vapor [3–5].

Several adsorbed species in the NO_x reduction have been observed by many researchers using infrared spectroscopy and intermediates such as isocyanate (–NCO) [6–8], organic nitro (R–NO_2) [9–12], nitrile or cyanide (–CN) [13–15], and ammonia [16] have been proposed to take part into the selective reduction of NO_x. However, consensus about the intermediates of NO_x reduction has not been obtained yet. Ukisu et al. [6,7] 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 with ethanol in the presence of water with the high productivity of a surface isocyanate intermediate even in the presence of water, and concluded 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 [8]. Additionally, in our recent studies, nitrogen-containing species (e.g., R–NO_2(a)) were also proposed as possible intermediates in the NO_x reduction with ethanol on Ag/Al_2O_3 [17]. Isocyanate species have been shown to generate from the decomposition of organic nitro compounds (R–NO_2) under a NO + O_2 + ethanol system [17]. Moreover, this reaction was found to be strongly influenced by catalyst support [18].

The present work is devoted to an investigation of the interaction of organic nitro compounds with supported silver catalysts. Particular attention is given to the effect of catalyst support in NO_x reduction activity and in isocyanate species formation by the thermal decomposition of nitromethane and nitroethane, which are employed as model organic nitro compounds (R–NO_2).

2. Experimental

Supported silver catalysts (2% by weight Ag: Ag/SiO_2, Ag/TiO_2, Ag/Al_2O_3) were prepared by an impregnation method described in previous papers [3,5]. The BET surface areas of Al_2O_3, TiO_2 and SiO_2 were 251, 100 and 35 m^2/g, respectively [5]. All reactant gases were high-purity chemical grade and were used without further purification. Ethanol, nitromethane and nitroethane were purified by freeze-pump-thaw techniques [8].

FT-IR spectra were recorded by a Nicolet Magna 550 spectrometer with a resolution of 4 or 8 cm^{-1} (200 scans), using a Pyrex glass IR cell equipped with a sample holder, electric heater and NaCl windows. The sample holder can be moved from the heater section to the window section

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in the IR cell. The samples for the IR measurement were prepared by the slurry method, similar to Ballinger and Yates [19]. The slurries of samples and distilled water were coated onto a tungsten grid. The net weight of the catalysts coated onto the grid was 10 mg (6.9 mg/cm^2). IR was measured using the same experimental procedure described in a previous paper [8].

The catalyst activity was measured in a fixed-bed flow reactor by passing a gas mixture of NO (1094 ppm), ethanol (884 ppm) and O_2 (10%) in He at a total flow rate of 100 ml/min over 0.2 g of catalyst (total pressure: 1 atm). The samples were pretreated with air at 500 °C for 2 h in a flow reactor, followed by He purge at room temperature. The formed N_2 during NO_x reduction by ethanol over supported silver catalysts was analyzed by an on-line gas chromatograph (Shimadzu GC-14A) equipped with molecular sieve 5A. The catalytic activity for NO reduction was evaluated by the percentage conversion of NO to N_2.

3. Results and discussion

3.1. Conversion of NO_x to N_2 over Ag/support catalysts

Figure 1 shows the conversion of NO_x to N_2 for the $NO + O_2 +$ ethanol system over supported silver catalysts. The Ag/Al_2O_3 catalyst showed extremely high NO_x conversion at a temperature range between 250 and 350 °C, while the catalytic activity of Al_2O_3 was lower than that of Ag/Al_2O_3 at temperatures below 450 °C. As shown in figure 1, the NO_x conversion to N_2 on Ag/TiO_2 (or TiO_2) and Ag/SiO_2 was much lower than that on Ag/Al_2O_3 (or Al_2O_3). The maximum values of NO_x conversion to N_2 over these catalysts were as follows: 86% (at 400 °C on Ag/Al_2O_3), 68% (at 450 °C on Al_2O_3), 18% (at 400 °C on Ag/TiO_2), 10% (at 400 °C on TiO_2) and 4% (at 350 °C on Ag/SiO_2). These results indicate that the NO_x conversion with ethanol strongly depends on the support and the presence of silver. It should be noted that temperatures higher than 450 °C led to a drastic decrease in the conversion of NO_x to N_2, due to the preferential oxidation of ethanol occurring at high temperature in the presence of excess O_2 [3,5].

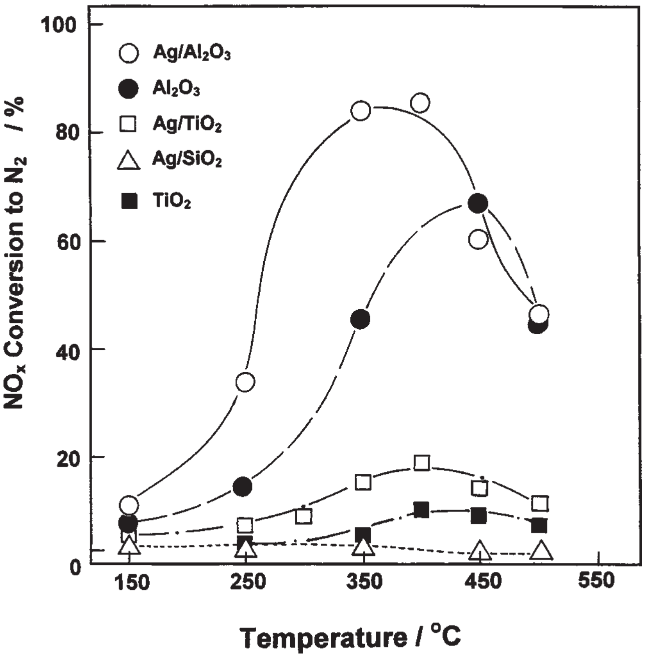

Figure 1. NO_x conversion to N_2 on supported silver catalysts and catalyst supports. Reaction conditions: NO (1094 ppm), ethanol (884 ppm) and O_2 (10%), balance He. Space velocity: 9550 h^{-1}.

3.2. Thermal decomposition of nitromethane and nitroethane on different Ag/support catalysts

The differences in NO_x conversion among these catalysts are discussed with respect to the behavior of surface NCO(a), nitromethane and nitroethane species on the basis of IR spectroscopic measurements. Organic nitro compounds ($R–NO_2$) and surface isocyanate (NCO(a)) are possible intermediate species in the selective reduction of NO_x with ethanol over Ag/Al_2O_3 ($NO + O_2 +$ ethanol system) [17,18]. In order to investigate the role of organic nitro compounds in the formation of the surface NCO(a) species, IR spectroscopy studies of model organic nitro molecules (e.g., nitromethane (CH_3NO_2) and nitroethane ($C_2H_5NO_2$)) were carried out on different supported silver catalysts.

Figure 2 shows the change of IR bands of adsorbed species on Ag/Al_2O_3, Ag/TiO_2 and Ag/SiO_2 catalysts, which were exposed to CH_3NO_2 (5 Torr) at room temperature and heated stepwise up to 350 °C at 10 °C/min. The strong bands at 1570–1560, 1410–1400 and 1385–1375 cm^{-1} are assigned to $\nu_a(NO_2)$, $\nu_s(NO_2)$ and $\delta_s(CH_3)$ of CH_3NO_2, respectively [20,21]. As shown in figure 2, raising the temperature to 250 °C led to a decrease of CH_3NO_2(a) bands and simultaneous appearance of new bands at 2260, 2161 cm^{-1} on Ag/Al_2O_3 and at 2204, 2135 cm^{-1} on Ag/TiO_2, while the IR bands of adsorbed nitromethane on Ag/SiO_2 were hardly affected by the heating process. The band at 2260 cm^{-1} on Ag/Al_2O_3 and the band at 2204 cm^{-1} on Ag/TiO_2 were in good agreement with the bands of Al–NCO on Ag/Al_2O_3 and Ti–NCO on Ag/TiO_2, respectively, formed under the $NO + O_2 +$ ethanol reaction system [18]. Similar assignments of NCO(a) on various oxide-supported noble metal catalysts such as M/Al_2O_3, M/TiO_2 and M/SiO_2 ($M =$ Pt, Pd, etc.) have been presented by Solymosi et al. [22,23]. Compared with Al–NCO species, Ti–NCO species were less stable and mostly decomposed during heating at 350 °C (figure 2). A similar phenomenon was reported by Solymosi et al. for the NCO(a) on TiO_2 [24]. The bands at 1663 and 1656 cm^{-1} are tentatively assigned here to ν(ONO) of organic nitrite compounds (R–ONO) on Ag/Al_2O_3 and Ag/TiO_2, respectively [9]. These species may have been formed by an isomerization of CH_3NO_2 (a) on the catalyst surface under the heating conditions. The bands at 2161 and 2135 cm^{-1} may be assigned to the CN stretching band of CN(a) and/or HCN(a) on Ag/Al_2O_3 and Ag/TiO_2, respectively [17]. In

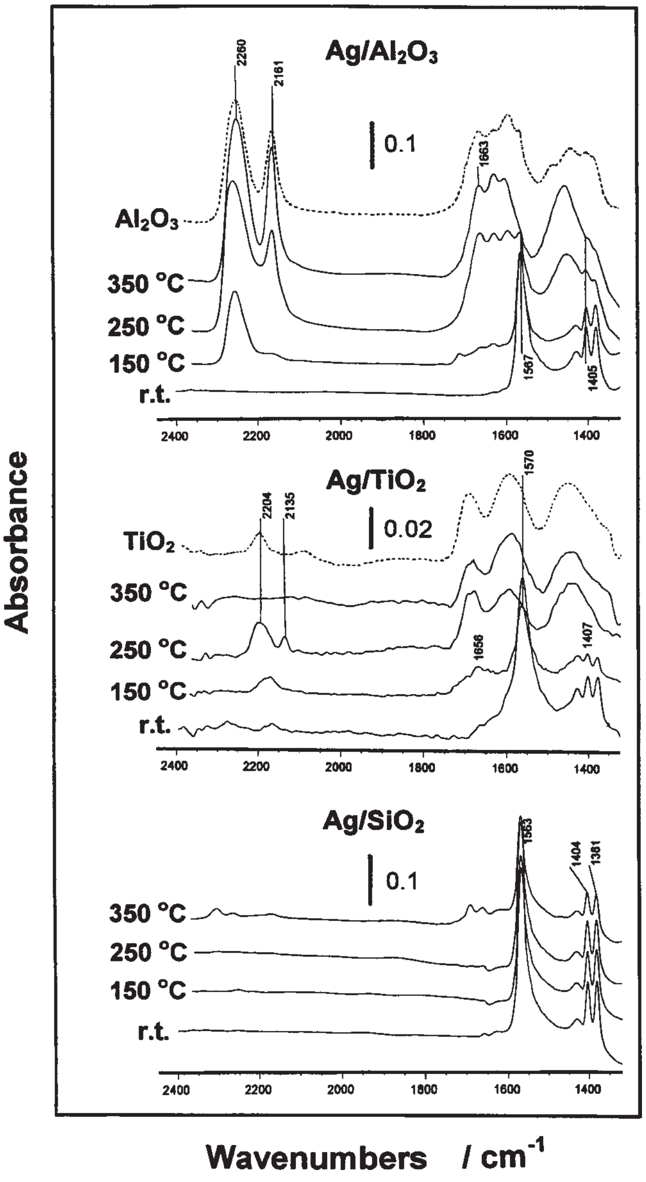

Figure 2. IR spectra of the surface species during the thermal decomposition of nitromethane (5 Torr) on Ag/support catalysts and supports alone. The dotted lines indicate the surface species on Al_2O_3 and TiO_2 at 250 °C.

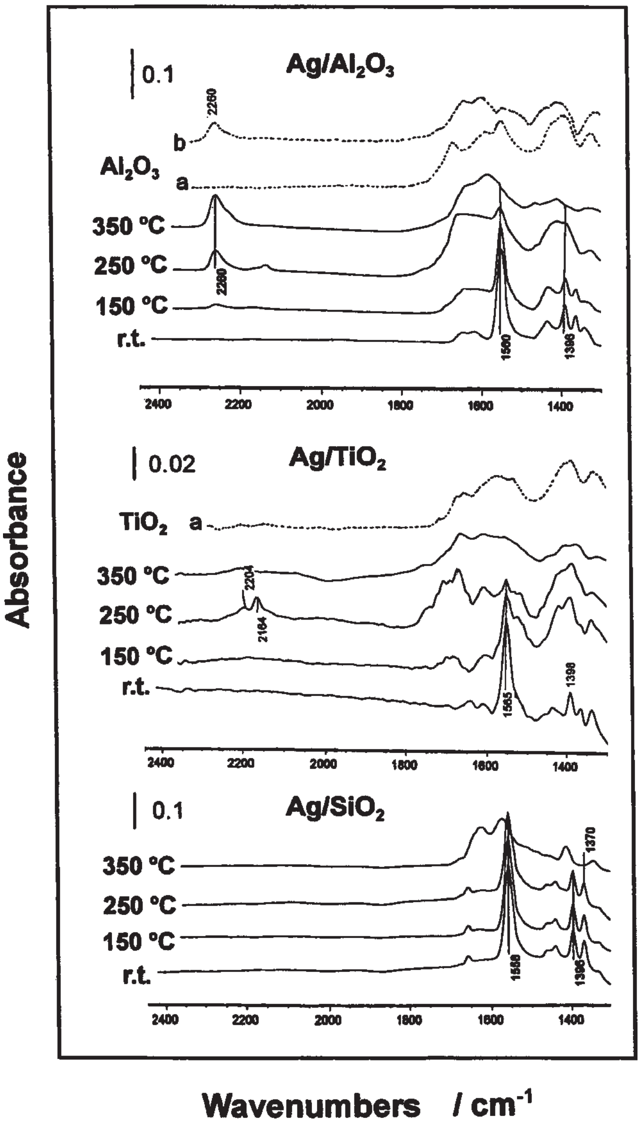

Figure 3. IR spectra of the surface species during the thermal decomposition of nitroethane (5 Torr) on Ag/support catalysts and supports alone. The dotted lines indicate the surface species on support alone at (a) 250 °C and (b) 350 °C.

fact, HCN was detected in the study of nitromethane decomposition over Co-ZSM-5 by Cant et al. [25]. These results suggest that the reaction step (1) takes place on Ag/Al_2O_3 and Ag/TiO_2 catalysts by means of the thermal decomposition of CH_3NO_2:

$$CH_3NO_2(a) \rightarrow \left[\text{–NCO(a)}\right] \qquad (1)$$

A nitromethane adsorption experiment was carried out using the supports alone (Al_2O_3 and TiO_2). As shown in figure 2 (dotted lines), IR spectra similar to the above were observed during the thermal decomposition at 250 °C. This result indicates that silver does not play a major role in the NCO(a) formation, therefore, this reaction occurs mainly on an oxide support surface (e.g., Lewis acid site).

The same set of experiments was performed with nitroethane ($C_2H_5NO_2$), which is also considered a possible form of R–NO_2 species in the NO_x reduction by ethanol, on the supported silver catalysts. Figure 3 shows the change of IR bands of adsorbed nitroethane on Ag/Al_2O_3, Ag/TiO_2 and Ag/SiO_2 following the same experimental procedure performed with nitromethane. Exposure of the catalyst samples to the nitroethane (5 Torr) at room temperature resulted in the appearance of strong bands at 1565–1555, 1405–1395 and 1380–1370 cm^{-1} due to adsorbed $C_2H_5NO_2$. As shown in figure 3, raising the temperature to 250 °C led to a decrease of $C_2H_5NO_2$(a) bands accompanied by the appearance of NCO(a) bands at 2260 cm^{-1} (Ag/Al_2O_3) and at 2204 cm^{-1} (Ag/TiO_2); however, no NCO(a) band was observed on Ag/SiO_2. Thus, the thermal decomposition of adsorbed nitroethane species apparently proceeds in the same way as nitromethane species (reaction step (2)):

$$C_2H_5NO_2(a) \rightarrow \left[\text{–NCO(a)}\right] \qquad (2)$$

Nevertheless, it should be noted that the NCO(a) formation by thermal decomposition of nitroethane on catalyst support alone (without silver) was significantly suppressed (figure 3, dotted line). This result indicates that silver may promote the activation of $C_2H_5NO_2$ by a scission of C–C bonds and/or the rearrangement reaction to NCO(a). Compared with the NCO(a) formation by nitromethane decomposition, the NCO(a) formation by nitroethane decomposition did not proceed efficiently. Consequently, this suggests that nitroethane is less reactive than nitromethane for NCO(a) species formation.

We consider the isocyanate species to be a key intermediate in the selective reduction of NO_x with ethanol on supported silver catalysts [8,17,18]. The stability and reactivity of NCO(a) should be discussed to explain why the NO_x conversion depends on the catalyst support. The NCO(a) species on Ag/Al_2O_3 was stable even at 400 °C in a vacuum [8,18], while on Ag/TiO_2, it had less thermal stability [18,24] and disappeared below 350 °C (figure 2). It should be noted that the selective reduction of NO_x with ethanol on supported silver catalysts occurred efficiently at 350–450 °C (figure 1). Therefore, the high thermal stability of NCO(a) on Ag/Al_2O_3, as compared with NCO(a) on Ag/TiO_2, may be correlated to the high efficiency of NO_x selective reduction with ethanol. As reported previously [6,26], NCO(a) on alumina-supported metal catalysts such as Cu/Al_2O_3 and Ag/Al_2O_3 reacted with NO, O_2 or $NO + O_2$ below 350 °C to produce N_2, CO_2 and CO (reaction step (3)):

$$\left[\text{–NCO(a)}\right] + \text{NO and/or } O_2 \rightarrow N_2 + CO_x \quad (x = 1, 2) \qquad (3)$$

In addition, Okuhara et al. [12] reported that organic nitro and isocyanate species were highly reactive with 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. We are currently undertaking further investigations with respect to the reactivity of NCO species on Ag/support catalysts with NO, $NO + O_2$ and H_2O using mass spectroscopy in our laboratory [27].

4. Conclusion

The present study revealed the formation of the NCO(a) species by decomposition of model organic nitro molecules (e.g., CH_3NO_2 and $C_2H_5NO_2$) on different supported silver catalysts. This behavior was strongly influenced by catalyst support. Moreover, the NO_x conversion in the selective reduction of NO_x with ethanol on supported silver catalysts was also found to be strongly dependent on the catalyst support. This suggests that the efficiency of supported silver catalyst in NO_x reduction with ethanol may be correlated with the nature of the NCO(a) species (e.g., stability, reactivity) which was formed by the decomposition of organic nitro compounds.

Acknowledgement

SK is grateful to the Japan Science and Technology Corporation (JST) for its financial support.

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