CHINESE JOURNAL OF CATALYSIS
Volume 27, Issue 11, November 2006
Online English edition of the Chinese language journal

Cite this article as: Chin J Catal, 2006, 27(11): 993–998.

RESEARCH PAPER

Mechanistic Study of Selective Catalytic Reduction of NO_x with C_2H_5OH and CH_3OCH_3 over Ag/Al_2O_3 by in Situ DRIFTS

WU Qiang, YU Yunbo, HE Hong*

State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

Abstract: Although C_2H_5OH and CH_3OCH_3 are isomeric compounds, C_2H_5OH is much more efficient for NO_x reduction than CH_3OCH_3. In situ diffuse reflectance infrared Fourier transform spectroscopy was used to study the reaction mechanism. The enolic species derived from the partial oxidation of C_2H_5OH over Ag/Al_2O_3 plays a crucial role in the formation of –NCO species during the selective catalytic reduction (SCR) of NO_x by C_2H_5OH. The high reactivity of the enolic species results in high surface concentration of –NCO species and high efficiency of NO_x reduction when C_2H_5OH was used as the reductant. In the case of CH_3OCH_3, the formate species as the main intermediate has low activity for the formation of –NCO species, which results in the relatively low efficiency during the SCR of NO_x.

Key Words: silver; alumina; nitrogen oxide; selective catalytic reduction; ethanol; methyl ether; in situ diffuse reflectance infrared Fourier transform spectroscopy; enolic species; formate species; isocyanate species

Since the first discovery of the high activity of Cu-ZSM-5 in the selective catalytic reduction (SCR) of NO_x by hydrocarbons [1], many studies have been carried out on this subject. Recently, Ag/Al_2O_3 has been investigated as a promising catalyst, which shows a relatively high activity for the SCR of NO_x by hydrocarbons or oxygen-containing organic compounds in the presence of excess O_2 [2–8]. Previous work showed that the Ag/Al_2O_3-C_2H_5OH system has a very high activity for the SCR of NO_x even in the presence of SO_2 and H_2O [4, 5].

It is well known that the reaction mechanism and the rate-determining step of the SCR of NO_x depend on the type of the catalyst, the component of the reagent, the type of the reductant, and the reaction conditions. So far, researchers believed that the –NCO species acts as the key intermediates during the SCR of NO_x [4, 5, 9–11]. Recently, He et al. [12] studied the mechanism of the SCR of NO_x by C_2H_5OH over Ag/Al_2O_3 and proposed that a surface enolic species RCH=CH–O$^-$, which is derived from the partial oxidation of C_2H_5OH, plays a crucial role in the formation of the –NCO species.

As C_2H_5OH and CH_3OCH_3 are isomeric compounds, it is of great significance to establish if the SCR of NO_x by CH_3OCH_3 follows the same mechanism as that of C_2H_5OH. To obtain further theoretical information with regard to the highly efficient catalyst-reductant system, it is important to investigate the different reaction mechanisms of the SCR of NO_x for both cases. In this study, in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was used to compare the different roles of C_2H_5OH and CH_3OCH_3 in the SCR of NO_x over Ag/Al_2O_3. Emphasis was placed on studying the formation, the role, and the activity of the surface adsorbed species on the catalyst, which would provide a better understanding of the mechanism of the SCR of NO_x for each case and help to design highly efficient systems for the SCR of NO_x.

1 Experimental

1.1 Preparation and activity test of the catalyst

The 4% Ag/Al_2O_3 catalyst was prepared by an impregnation method according to the literature [6]. The catalytic activity was measured in a fixed-bed reactor by passing a gaseous mixture of 0.08% NO, 0.1565% reductant, and 10% O_2 in

---

Received date: 2006-04-27.

*** Corresponding author.** Tel: +86-10-62849123; Fax: +86-10-62849123; E-mail: honghe@rcees.ac.cn

Foundation item: Supported by the National Natural Science Foundation of China (20437010).

N_2 balance at a total flow rate of 2 L/min over 0.6 g catalyst ($W/F = 0.018$ (g·s)/ml, GHSV = 50000 h^{-1}). An aqueous C_2H_5OH solution was fed into the gas stream using a syringe pump and vaporized using a coiled heater at the inlet of the reactor. NO_x conversion was analyzed online using a chemiluminescence $NO/NO_2/NO_x$ analyzer (42C-HL, Thermo Environmental Instruments Inc.).

1.2 In situ DRIFTS analysis

In situ DRIFTS spectra were recorded on a NEXUS 670 FT-IR spectrometer equipped with a smart collector and an MCT/A detector cooled by liquid N_2. The catalyst (0.03 g) was finely ground and placed in a ceramic crucible. Prior to each experiment, the catalyst was heated to 873 K in a flow of 10% O_2/N_2 for 60 min and then cooled to the desired temperature. A spectrum of the catalyst in the flow of $N_2 + O_2$ was taken as the background. The overall gas flow rate was 300 ml/min. All the spectra were measured at a resolution of 4 cm^{-1} with an accumulation of 100 scans.

2 Results and discussion

2.1 Comparison of the catalytic activity of Ag/Al_2O_3 during the SCR of NO_x by C_2H_5OH and CH_3OCH_3

Fig. 1 compares the reduction of NO_x by C_2H_5OH and CH_3OCH_3 over the Ag/Al_2O_3 catalyst. When C_2H_5OH was used as the reductant, NO_x was reduced effectively within the whole temperature range, and the maximum NO_x conversion was 99.6% at 690 K. In contrast, there was a relatively low NO_x conversion using CH_3OCH_3 in the whole reaction temperature range, and the highest conversion of NO_x was only 22.5%. These results indicate that the NO_x conversion is strongly influenced by the structure of the reductants. It has been widely accepted that hydrocarbon activity in the SCR of NO_x increases with the number of carbon atoms and the degree of unsaturation [13]. Although C_2H_5OH and CH_3OCH_3 are isomeric compounds, CH_3OCH_3 is less effective compared with C_2H_5OH for the SCR of NO_x. This difference can be explained on the basis of different mechanisms for each case and it is described in the following sections.

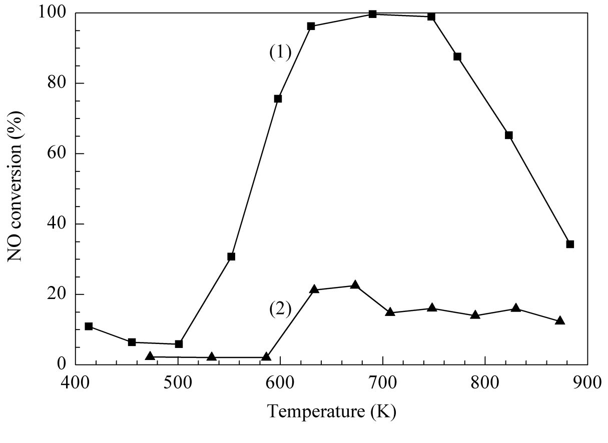

Fig. 1 Comparison of the catalytic activity of Ag/Al_2O_3 during the selective catalytic reduction (SCR) of NO_x by C_2H_5OH (1) and CH_3OCH_3 (2) at various temperatures

(Reaction conditions: $\varphi(NO) = 0.08\%$, $\varphi(C_2H_5OH) = \varphi(CH_3OCH_3) = 0.1565\%$, $\varphi(O_2) = 10\%$, N_2 balance.)

2.2 In situ DRIFTS study of the SCR of NO_x by C_2H_5OH and CH_3OCH_3 over Ag/Al_2O_3

The difference in behavior between C_2H_5OH and CH_3OCH_3 for the SCR of NO_x over Ag/Al_2O_3 was investigated using the in situ DRIFTS method. The in situ DRIFTS spectra of Ag/Al_2O_3 were recorded at various temperatures in a steady state after exposing Ag/Al_2O_3 to $NO + O_2 + C_2H_5OH$ or to $NO + O_2 + CH_3OCH_3$. The reaction conditions are the same as those in the measurement of activity.

Fig. 2(a) shows the in situ DRIFTS spectra of the Ag/Al_2O_3 catalyst in a flow of $NO + O_2 + C_2H_5OH$. It can be seen that several peaks appeared in the region of 1700–1300 cm^{-1}. Based on the previous study [12, 14], the bands at 1585 and 1304 cm^{-1} are due to the adsorbed bidentate nitrate species (NO_3^-), and the peaks at 1579 and 1468 cm^{-1} are associated with the acetate species (CH_3COO^-), while the peaks at 1633, 1416, and 1336 cm^{-1} are assigned to the enolic species ($RCH{=}CH{-}O^-$), which was predominantly formed due to the partial oxidation of C_2H_5OH. Furthermore, a very strong peak appeared at 2233 cm^{-1}, which is assigned to the –NCO species. It has been widely accepted that –NCO species is the key intermediate in the SCR of NO_x over Ag/Al_2O_3, and its high productivity results in the high efficiency of NO_x reduction [9–12, 14]. As can be seen from Fig. 2(a), the intensities of nitrate species and enolic species decreased gradually with the increase in reaction temperature, while the intensity of –NCO species increased gradually with the reaction temperature. At 673 K, the intensity of –NCO species reached the maximum, indicating that the system underwent a quick and efficient reaction, which is in good agreement with the results of the activity study.

Fig. 2(b) represents the in situ DRIFTS spectra of the Ag/Al_2O_3 catalyst in a flow of $NO + O_2 + CH_3OCH_3$ in a steady state at various temperatures. Unlike the C_2H_5OH-containing system, when the Ag/Al_2O_3 catalyst was exposed to a $NO + O_2 + CH_3OCH_3$ mixture under the same experimental conditions, the peak due to the enolic species (around 1633 cm^{-1}) was not observed, whereas very strong peaks appeared at 1591 and 1379 cm^{-1}, which are assigned to $\nu_{as}(OCO)$ and $\nu_s(OCO)$ of formate species, respectively. In addition, the peaks at 1585 and 1304 cm^{-1} are attributed to the bidentate nitrate species, and the peak at 1562 cm^{-1} corresponds to the monodentate nitrate species, while the peaks at