

Effect of hydrogen on reaction intermediates in the selective catalytic reduction of NO_x by C_3H_6

Xiuli Zhang, Yunbo Yu, Hong He*

State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, P.O. Box 2871, 18 Shuangqing Road, Beijing 100085, PR China

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Abstract

Selective catalytic reduction of NO_x by C_3H_6 in the presence of H_2 over $\text{Ag}/\text{Al}_2\text{O}_3$ was investigated using in situ DRIFTS and GC–MS measurements. The addition of H_2 promoted the partial oxidation of C_3H_6 to enolic species, the formation of $-\text{NCO}$ and the reactions of enolic species and $-\text{NCO}$ with NO_x on $\text{Ag}/\text{Al}_2\text{O}_3$ surface at low temperatures. Based on the results, we proposed reaction mechanism to explain the promotional effect of H_2 on the SCR of NO_x by C_3H_6 over $\text{Ag}/\text{Al}_2\text{O}_3$ catalyst.

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1. Introduction

Emission control of NO_x from diesel and lean-burn engine exhausts remains one of the major challenges for environmental catalysis. As a highly promising technology, selective catalytic reduction (SCR) of NO_x with various reductants has been extensively studied. Among a number of catalysts, alumina-supported silver ($\text{Ag}/\text{Al}_2\text{O}_3$) catalyst shows a very high activity for NO_x reduction by alcohols [1,2] or higher hydrocarbons [3–5]. Nevertheless, this catalyst shows a low activity at temperatures below *ca.* 700 K for the SCR of NO_x by lower hydrocarbons, and this becomes a major disadvantage for practical use of this technology. A recent study found that addition of H_2 to feed stream could result in a remarkable improvement in the activity of NO_x reduction and the active temperature range [6]. Furthermore, the positive effect of H_2 is found to be specific for silver catalysts such as $\text{Ag}/\text{Al}_2\text{O}_3$ [6–8] and Ag-zeolites [9–11]. The effect of H_2 for the SCR of NO_x over $\text{Ag}/\text{Al}_2\text{O}_3$ catalyst has been investigated with several alkanes (e.g. propane, octane, decane). Using in situ FTIR spectroscopy, the promotional effect of H_2 on the oxidation of NO to NO_2 and the oxidation

of hydrocarbons to acetates has been revealed on $\text{Ag}/\text{Al}_2\text{O}_3$ [12–14]. Instead of NO oxidation, Shibata et al. [9–11] proposed that the positive effect of H_2 addition on the NO_x reduction was attributed to the formation of small charged metallic $\text{Ag}_n^{\delta+}$ clusters based on the results of UV–vis spectroscopy. Burch and Breen et al. [15,16] postulated that the improvement of added H_2 in the SCR of NO_x was due to the formation of $\text{C}=\text{N}$ species, and was not associated with significant structural changes in the $\text{Ag}/\text{Al}_2\text{O}_3$ catalyst at low temperatures.

Based on our previous DRIFTS studies and DFT calculations, a novel mechanism of the SCR of NO_x by $\text{C}_2\text{H}_5\text{OH}$ or C_3H_6 over $\text{Ag}/\text{Al}_2\text{O}_3$ was proposed in the absence of H_2 [17,18]. As an important intermediate, an enolic species originated from partial oxidation of $\text{C}_2\text{H}_5\text{OH}$ or C_3H_6 was identified over $\text{Ag}/\text{Al}_2\text{O}_3$. The high surface concentration of enolic species is related with a high surface concentration of $-\text{NCO}$ species and a high efficiency of NO_x reduction by $\text{C}_2\text{H}_5\text{OH}$, whereas a low concentration of enolic species corresponds to a low efficiency for the NO_x reduction by C_3H_6 over $\text{Ag}/\text{Al}_2\text{O}_3$.

The promotional effect of H_2 on the formation of enolic species during the hydrocarbon oxidation on $\text{Ag}/\text{Al}_2\text{O}_3$ catalyst has not been reported. This paper reports an effect of H_2 on the reduction of NO_x by C_3H_6 over $\text{Ag}/\text{Al}_2\text{O}_3$ catalyst within low temperature region. The role of H_2 on the

* Corresponding author. Tel.: +86 10 62849123; fax: +86 10 62923563.

E-mail address: honghe@rcees.ac.cn (H. He).

formation of intermediates on the Ag/Al₂O₃ surface, especially enolic species, was investigated using in situ DRIFTS. The analysis was also based on monitoring of the products in gas phase using GC–MS under the reaction conditions.

2. Experimental

2.1. Catalyst preparation

The catalyst used in this work was an alumina-supported silver catalyst (4% Ag/Al₂O₃), prepared by an impregnation of γ -Al₂O₃ powder (200 m²/g) with an appropriate amount of silver nitrate aqueous solution. The sample was dried at 393 K overnight and calcined at 873 K for 3 h in air. The catalyst was sieved into 20–40 meshes before use.

2.2. Catalytic tests

The measurement of catalytic activity of Ag/Al₂O₃ was carried out in a fixed-bed reactor connected with a temperature controller. The typical experiment condition was as follows. The feed gas stream consisted of 800 ppm NO, 1714 ppm C₃H₆, 10% O₂, 0–1% H₂, and N₂ as balance. The total gas flow rate was 2000 cm³ min⁻¹ over 0.6 g catalyst ($W/F = 0.018$ g s cm⁻³, GHSV = $\sim 50,000$ h⁻¹). NO_x conversion was analyzed on-line by a chemiluminescence NO/NO₂/NO_x analyzer (42C-HL, Thermo Environmental Instrument Inc.).

2.3. Analysis of gas products

The analysis of C₃H₆ was carried out using gas chromatography (Agilent 6890 N GC) equipped with Porapak Q column. Other gas products were analyzed by a NEXUS 670-FTIR fitted with a gas cell of 0.2 dm³ and gas chromatography (Agilent 6890 N GC) coupled to a mass spectrometer (Agilent 5973 N MS) with a column-containing HP-PLOT Q (Agilent 30 m \times 0.32 mm, 20 μ m film), respectively. All gas FT-IR spectra were measured with a resolution of 0.5 cm⁻¹ and with an accumulation of 16 scans.

2.4. In situ DRIFTS

In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) spectra were recorded on a Nexus 670 (Thermo Nicolet) FT-IR, equipped with an in situ diffuse reflection chamber and a high sensitivity MCT/A detector cooled by liquid nitrogen. The Ag/Al₂O₃ catalyst for in situ DRIFTS study was finely ground and placed into a ceramic crucible. Prior to recording each DRIFTS spectrum, Ag/Al₂O₃ catalyst was heated in situ in 10% O₂ + N₂ flow for 60 min at 573 K and 873 K, respectively, and then cooled to the desired temperature for taking the reference spectrum. All gas mixtures were fed at a flow rate of 300 cm³ min⁻¹. All spectra were measured with a resolution of 4 cm⁻¹ and with an accumulation of 100 scans.

3. Results

3.1. Effect of H₂ addition on the SCR of NO_x by C₃H₆ over Ag/Al₂O₃

Fig. 1A shows the conversions of NO_x for the C₃H₆-SCR with or without 1% H₂ over Ag/Al₂O₃ catalyst as a function of temperature. The NO_x conversion in the absence of H₂ was less than 10% within the temperature range from 423 K to 573 K, and the maximum NO_x conversion of 97% was achieved at 723 K. Clearly, the addition of H₂ significantly enhanced NO_x conversion, especially in the temperature range of 473–623 K. The NO_x conversion was elevated up to 89% at 490 K, and it was then kept above 90% over a wide temperature range of 500–750 K. In the temperature region greater than 723 K, the NO_x conversion trend was almost same for the case with or without H₂. Fig. 1B shows the C₃H₆ conversions over Ag/Al₂O₃ in the presence or absence of H₂. The enhancement effect of H₂ on the NO_x reduction by C₃H₆ was also reflected in the high conversion of C₃H₆ at low temperatures. On-set temperature for C₃H₆ conversion with H₂ was shifted from 650 K to 470 K and

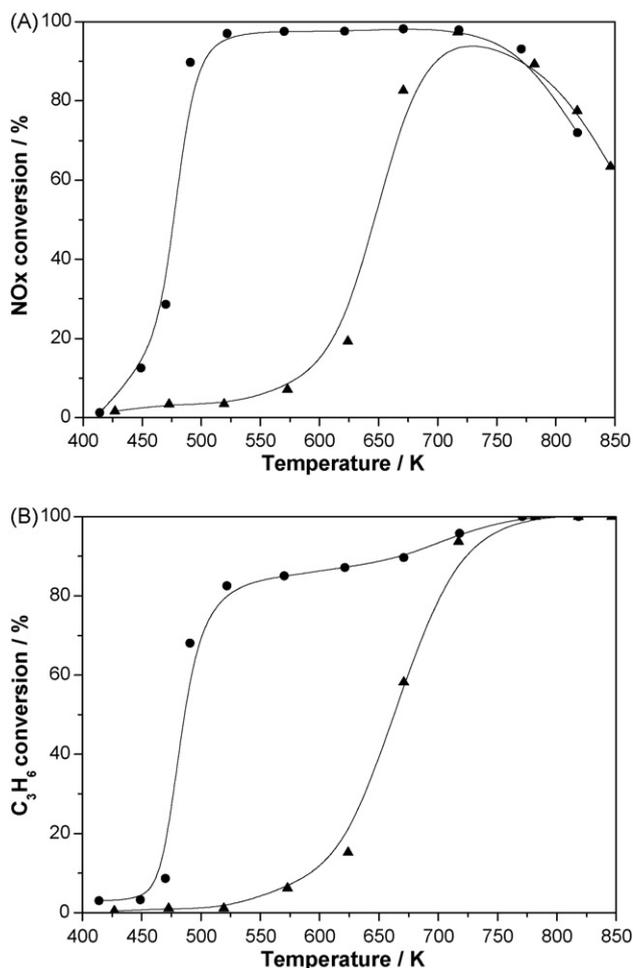


Fig. 1. NO_x conversion (A) and C₃H₆ conversion (B) for the SCR of NO_x by C₃H₆ over Ag/Al₂O₃ catalyst in the presence of 1% H₂ (●) and absence of H₂ (▲). Reaction conditions: NO, 800 ppm; C₃H₆, 1714 ppm; O₂, 10% in N₂ balance at total flow rate 2000 cm³ min⁻¹, GHSV = 50,000 h⁻¹.

the temperature for the complete conversion of C_3H_6 did not change regardless of the presence of H_2 .

The main products of the SCR of NO_x by hydrocarbons over Ag/Al_2O_3 catalyst were N_2 , CO_2 and H_2O , accompanied by the formation of various oxygen- and nitrogen-containing compounds as intermediates [2,18,19]. Previous studies pointed out that the reaction pathway of NO_x reduction was relative to the oxygen- and nitrogen-containing intermediates [20]. Fig. 2A and B show the GC–MS chromatograms of the gas phase products of the SCR of NO_x by C_3H_6 over Ag/Al_2O_3 in the absence or presence of H_2 at 473 K in the steady state, respectively. In the absence of H_2 , despite small amounts of H_2O and CO_2 detected along with unreacted C_3H_6 and C_3H_8 , there was no other oxygen- and nitrogen-containing compounds observed at 473 K (Fig. 2A). Unlike the case without H_2 , the presence of H_2 resulted in the appearance of partial oxidation products of C_3H_6 , such as acetaldehyde and acrolein in a flow of $NO + C_3H_6 + O_2 + H_2$ at 473 K (Fig. 2B). Traces of CH_3CN and CH_3NO_2 were detected as nitrogen-containing products in Fig. 2B. In addition, small amount of N_2O (<10 ppm) and traces of $HCHO$ (<25 ppm) were also detected according to the integrated peak range from FTIR gas spectra at 473 K (data not shown). Considering the conversions of NO_x and C_3H_6 at 473 K

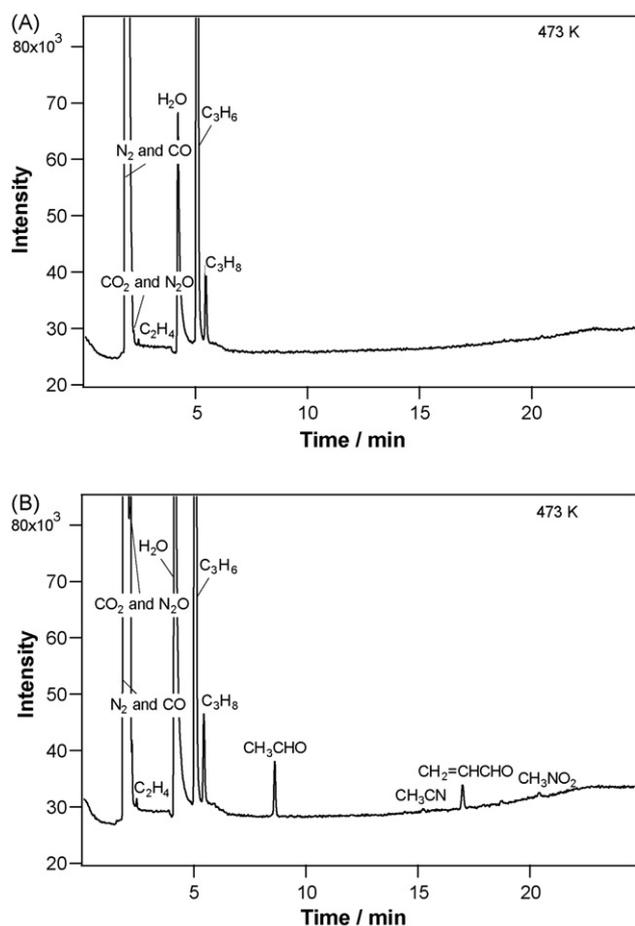


Fig. 2. GC–MS chromatogram of gas products of $NO + C_3H_6 + O_2$ reaction in the absence of H_2 (A) and presence of 1% H_2 (B) at 473 K over Ag/Al_2O_3 catalyst. Reaction conditions: NO , 800 ppm; C_3H_6 , 1714 ppm; O_2 , 10% in N_2 balance at total flow rate $2000 \text{ cm}^3 \text{ min}^{-1}$, GHSV = $50,000 \text{ h}^{-1}$.

in Fig. 1A and B, these GC–MS results were reasonable. At temperature above 573 K, no significant difference in the varieties of oxygen- and nitrogen-containing compounds was found during the NO_x reduction by C_3H_6 in the presence and absence of H_2 (data not shown).

3.2. Formation of partial oxidation products of C_3H_6 in the absence and presence of H_2 over Ag/Al_2O_3

The effect of hydrogen on the formation of oxygenated hydrocarbon species was studied by in situ DRIFTS at various temperatures (423–773 K). Fig. 3A and B show the in situ DRIFTS spectra of Ag/Al_2O_3 catalyst in a flow of $C_3H_6 + O_2$ with or without the addition of H_2 in a steady state. As shown in Fig. 3A, many peaks appeared on Ag/Al_2O_3 after exposure to a flow of $C_3H_6 + O_2$. The bands at 1577 cm^{-1} and 1460 cm^{-1} are

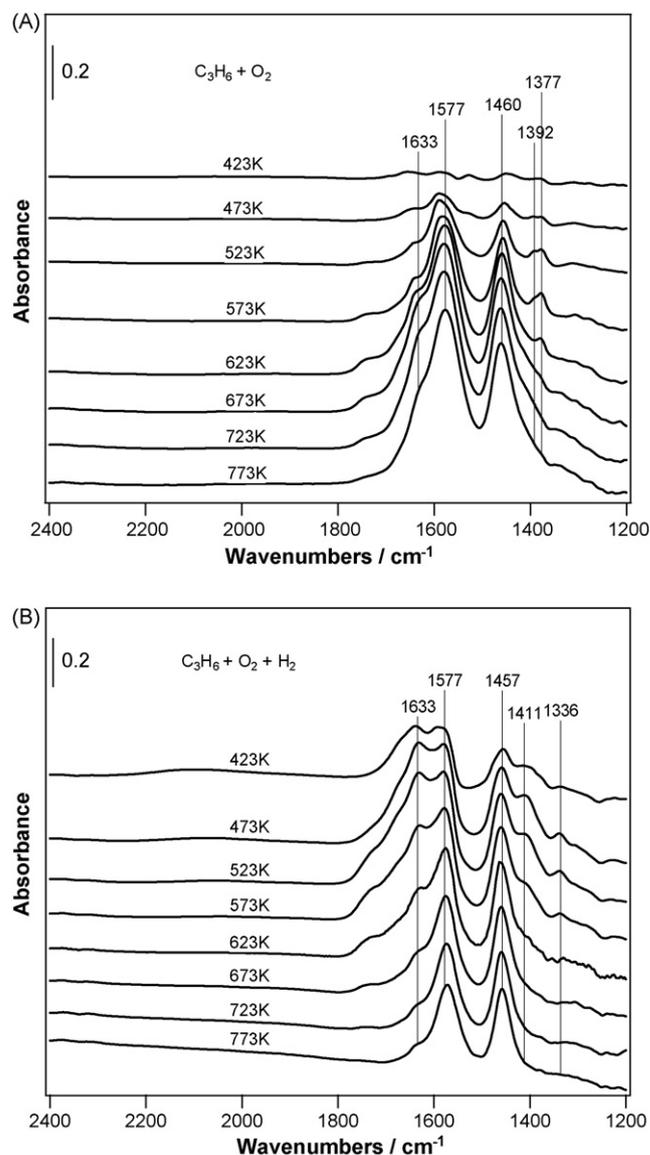


Fig. 3. In situ DRIFTS spectra of Ag/Al_2O_3 in a steady state at various temperatures in a flow of $C_3H_6 + O_2$ in the absence (A) and presence of 1% H_2 (B). Conditions: C_3H_6 , 1714 ppm; O_2 , 10%; N_2 balance.

attributed to ν_{as} (OCO) and ν_{s} (OCO) of adsorbed acetate, respectively [3,4,21,22], and the peaks at 1392 cm^{-1} and 1377 cm^{-1} are assigned to δ ($-\text{CH}_3$) and δ ($-\text{CH}_2$) of adsorbed acetate [4]. A shoulder peak at 1633 cm^{-1} appeared at 623 K, and its intensity increased gradually with increasing temperature from 623 K to 723 K and then decreased with further increasing temperature. Based on our previous studies [17,18], the peak at 1633 cm^{-1} could be assigned to ν_{as} (RCH=C–O) of a surface enolic species, which derived from the partial oxidation of C_3H_6 . In the case of $\text{C}_3\text{H}_6 + \text{O}_2$, acetate was predominant species on the surface of $\text{Ag}/\text{Al}_2\text{O}_3$ within the whole temperature region. When H_2 was added to a flow of $\text{C}_3\text{H}_6 + \text{O}_2$, a very strong peak at 1633 cm^{-1} attributed to enolic species was observed even at a temperature as low as 423 K (Fig. 3B). This peak was accompanied by the appearance of strong bands at 1457 cm^{-1} and 1577 cm^{-1} , which can be attributed to acetate. In addition, the peaks at 1411 cm^{-1} for ν_{s} (RCH=C–O) and 1336 cm^{-1} for δ (C–H) of the enolic species were also visible [17,18]. In contrast, neither enolic nor acetate species existed at 423 K in the absence of H_2 (Fig. 3A), strongly suggesting that the presence of H_2 enhanced the partial oxidation of C_3H_6 at low temperatures. In the case of $\text{C}_3\text{H}_6 + \text{O}_2 + \text{H}_2$, the enolic species (1633 cm^{-1} , 1411 cm^{-1} and 1336 cm^{-1}) and acetate species (1577 cm^{-1} and 1457 cm^{-1}) were predominant species in the low temperature range of 423–573 K, while the acetate species became dominant surface species on the $\text{Ag}/\text{Al}_2\text{O}_3$ during the partial oxidation of C_3H_6 in the presence of H_2 in the high temperature range of 623–773 K.

3.3. Steady state in situ DRIFTS study of the SCR of NO_x by C_3H_6 in the absence and presence of H_2 over $\text{Ag}/\text{Al}_2\text{O}_3$

In order to understand the effect of H_2 on the activity for the SCR of NO_x , we also investigated the formation and reactivity of surface species on the $\text{Ag}/\text{Al}_2\text{O}_3$ surface by DRIFTS method. Fig. 4A and B show the in situ DRIFTS spectra of $\text{Ag}/\text{Al}_2\text{O}_3$ catalyst in a flow of $\text{NO} + \text{C}_3\text{H}_6 + \text{O}_2$ with or without the addition of H_2 in a steady state at various temperatures. As shown in Fig. 4A, strong bands at 1554 cm^{-1} and 1232 cm^{-1} were observed and assigned to unidentate nitrates after exposure of the catalyst to $\text{NO} + \text{C}_3\text{H}_6 + \text{O}_2$ mixture gas at 423 K [4,23]. With the increase of temperature, the bidentate nitrates (1589 cm^{-1} and 1300 cm^{-1}) and the acetate (1574 cm^{-1} and 1460 cm^{-1}) appeared [3,4,21–23]. At 473 K, a small shoulder at 1637 cm^{-1} was observed and assigned to enolic species and its intensity increased with the increase of temperature. Raising the temperature from 623 K to 773 K, the enolic species (1637 cm^{-1}) and the bidentate nitrates (1300 cm^{-1}) decreased gradually. Meanwhile, a weak band at 2230 cm^{-1} assigned to isocyanate ($-\text{NCO}$) species appeared at 623 K [2,3,22–24], which reached its strongest intensity at 723 K. Compared with the enolic species, the acetate (1574 cm^{-1} and 1460 cm^{-1}) was still strong in the high temperature region. From these results, it is clear that the enolic species is more active than the acetate species for reaction with NO_3^- to form $-\text{NCO}$ [18]. In the presence of H_2 , the enolic species (1633 cm^{-1}) could be identified even at a

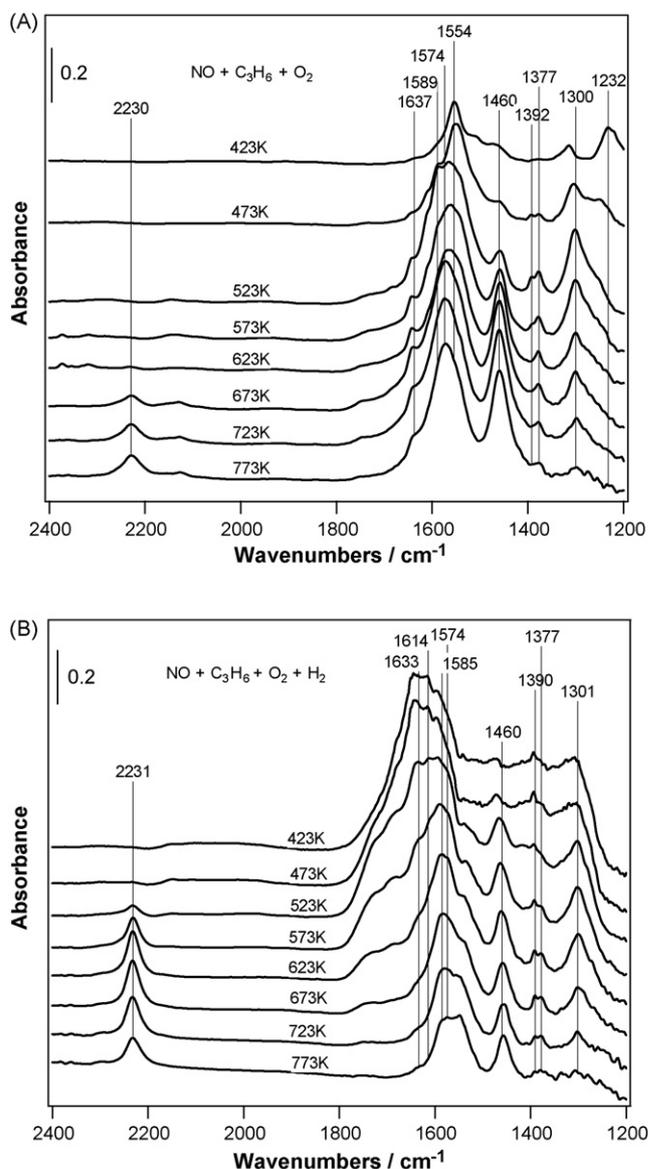


Fig. 4. In situ DRIFTS spectra of $\text{Ag}/\text{Al}_2\text{O}_3$ in a steady state at various temperatures in a flow of $\text{NO} + \text{C}_3\text{H}_6 + \text{O}_2$ in the absence (A) and presence of 1% H_2 (B). Conditions: NO , 800 ppm; C_3H_6 , 1714 ppm; O_2 , 10%; N_2 balance.

temperature as low as 423 K, and the intensity of the enolic species peak was the strongest among all the absorbed species peaks at 423 K (Fig. 4B). This result strongly suggests that the presence of H_2 facilitates the formation of enolic species during the NO_x reduction by C_3H_6 , and such facilitation was more significant at low temperatures. Compared with Fig. 4A, a new broad peak appeared around $1700\text{--}1750\text{ cm}^{-1}$, which indicates the formation of surface carbonyl species. With the increase of temperature from 473 K to 623 K, the enolic species disappeared promptly on the $\text{Ag}/\text{Al}_2\text{O}_3$ surface, and the relation between the formation of $-\text{NCO}$ species and consumption of enolic species became clear as shown in Fig. 4B. It is also noticeable that the appearance of $-\text{NCO}$ peak at 2231 cm^{-1} in Fig. 4B began at lower temperatures if comparing with the case of $\text{NO} + \text{C}_3\text{H}_6 + \text{O}_2$ in Fig. 4A, and the intensity of $-\text{NCO}$ peak

was much stronger than that in Fig. 4A over a wide temperature range of 523–773 K.

3.4. Reactivity of the surface intermediates over Ag/Al₂O₃

To further elucidate the reactivity of reaction intermediates, the transient response experiment of DRIFTS was carried out on the Ag/Al₂O₃ at 523 K. Figs. 5A and 6A show the dynamic changes of in situ DRIFTS spectra of the adsorbed species in a flow of NO + O₂ and NO + O₂ + H₂ after the Ag/Al₂O₃ catalyst was pre-exposed to a flow of NO + C₃H₆ + O₂ + H₂ for 60 min at 523 K, respectively. After switching the feed gas from a flow of NO + C₃H₆ + O₂ + H₂ to a flow of NO + O₂, the intensity of enolic species decreased gradually with time, accompanied with the increase in the concentration of –NCO species as

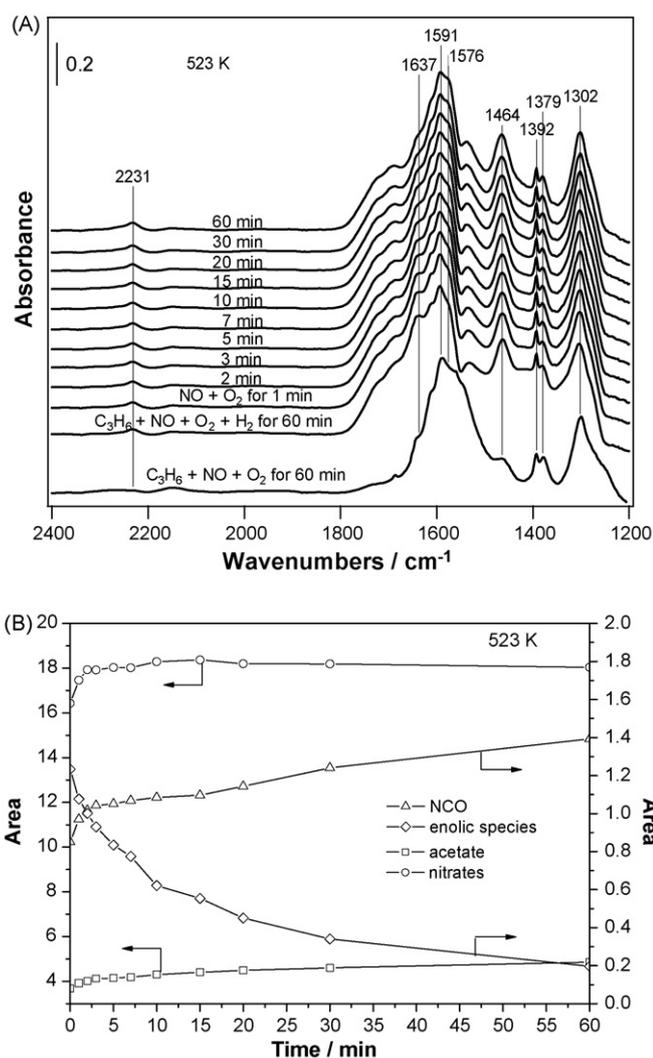


Fig. 5. (A) Dynamic changes of in situ DRIFTS spectra of adsorbed species on Ag/Al₂O₃ as a function of time in a flow of NO + O₂ at 523 K. Before measurement, the catalyst was pre-exposed to a flow of NO + C₃H₆ + O₂ + H₂ for 60 min at 523 K. The bottom spectrum was taken after the Ag/Al₂O₃ exposed to a flow of NO + C₃H₆ + O₂ for 60 min at 523 K. Conditions: NO, 800 ppm; O₂, 10%; N₂ balance. (B) Time dependence of the integrated areas of the peaks for different adsorbed species in (A): (△) –NCO, 2191–2305 cm⁻¹; (◇) enolic species, 1624–1660 cm⁻¹; (□) acetate, 1441–1497 cm⁻¹; (○) nitrates, 1250–1350 cm⁻¹.

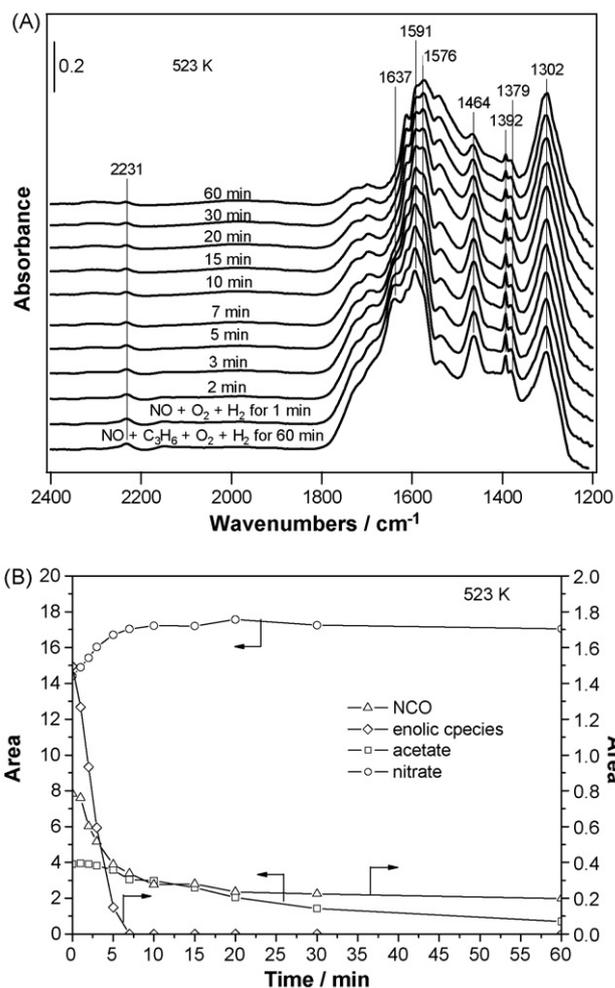


Fig. 6. (A) Dynamic changes of in situ DRIFTS spectra of adsorbed species on Ag/Al₂O₃ as a function of time in a flow of NO + O₂ + H₂ at 523 K. Before measurement, the catalyst was pre-exposed to a flow of NO + C₃H₆ + O₂ + H₂ for 60 min at 523 K. Conditions: NO, 800 ppm; O₂, 10%; H₂, 1%; N₂ balance. (B) Time dependence of the integrated areas of the peaks for different adsorbed species in (A): (△) –NCO, 2191–2305 cm⁻¹; (◇) enolic species, 1624–1660 cm⁻¹; (□) acetate, 1441–1497 cm⁻¹; (○) nitrates, 1250–1350 cm⁻¹.

shown in Fig. 5A. The integrated areas of these peaks in Fig. 5A are displayed as a function of time in Fig. 5B. The linkage between the formation of the –NCO species and the consumption of the enolic species suggests the participation of the enolic species in the formation of –NCO species. In contrast, the concentration of acetate increased slowly, which could originate from the further oxidation of the enolic species in a flow of NO + O₂. These results indicate that the enolic species has higher reactivity with NO + O₂ species than acetate species does. This is in agreement with our previous conclusion [18]. Compared with the case in Fig. 5A, we also monitored the evolution of the adsorbed species in a flow of NO + O₂ + H₂ as a function of time at 523 K (Fig. 6A). The integrated areas of these peaks in Fig. 6A are also displayed as a function of time in Fig. 6B. It can be seen in Fig. 6 that the peak of enolic species disappeared completely in 7 min, which indicates that the enolic species in a flow of NO + O₂ + H₂ was more active than that in a flow of NO + O₂. Contrary to the case in Fig. 5, the intensity of acetate lowered with time after the peak of enolic

species almost disappeared. Moreover, the intensity of $-NCO$ species also decreased. These results indicate that the presence of H_2 accelerates the reactions of enolic species and $-NCO$ towards $NO + O_2$ to form N_2 as a final product.

4. Discussion

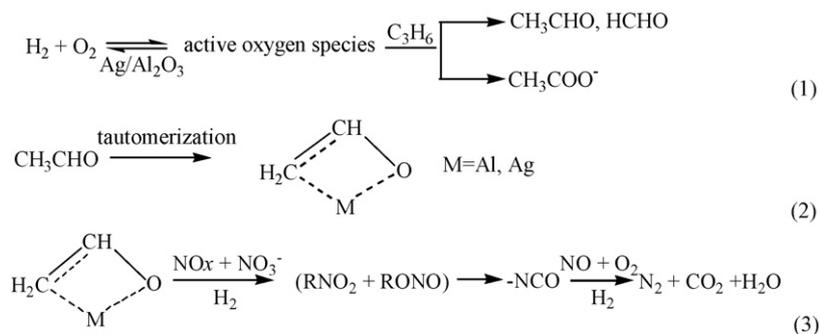
The reaction mechanism of the SCR of NO_x by C_3H_6 over Ag/Al_2O_3 has been proposed and summarized as follows: $NO + O_2 + C_3H_6 \rightarrow NO_x$ (nitrate in particular) + $C_xH_yO_z$ (acetate in particular) $\rightarrow R-ONO + R-NO_2 \rightarrow -NCO + -CN + NO + O_2 \rightarrow N_2 + CO_2$ [4,5,21,24–27]. Many research groups [24,26,27] proposed that the acetate played a crucial role in the formation of $-NCO$ species by reaction towards $NO + O_2$ at high temperatures. Recently, we found enolic species as an intermediate of partial oxidation of C_2H_5OH and C_3H_6 on Ag/Al_2O_3 , and believed that the enolic species has much higher reactivity than acetate towards $NO + O_2$ to form $-NCO$ species by in situ DRIFTS measurement [17].

In the present study, the conversion of NO was enhanced dramatically by the addition of H_2 at a low temperature range (473–623 K). The oxidation of C_3H_6 was also promoted during the $NO + C_3H_6 + O_2$ reaction in the presence of H_2 . There is a dramatic difference in the surface species concentration in the oxidation of C_3H_6 with and without H_2 (Fig. 3). The presence of H_2 clearly favors the partial oxidation and the formation of the enolic species over Ag/Al_2O_3 . Recently, the formation and promotion of enolic species by adding H_2 were also observed in partial oxidation of other light hydrocarbons (results not shown). Hayashi et al. [28] reported that the oxidation of C_3H_6 was enhanced by H_2 over $Au/TiO_2/SiO_2$ catalyst. They suggested that dioxygen might be transformed by the reduction with H_2 to an active species over the catalyst, which had the ability to selectively oxidize C_3H_6 to propene oxide. The promotional effect of H_2 on the partial oxidation was also found by several other authors using different hydrocarbons as reducing agents in the SCR of NO_x [8,14,15]. Richter et al. [8] speculated that molecular oxygen dissociates over small Ag^0 clusters formed by hydrogen reduction of appropriately sized Ag_2O , and promotes oxidation of hydrocarbons to oxygenates. Sazama et al. [14] proposed that H_2 took part in the SCR of NO_x by decane and reacted with oxygen to form hydroperoxy and hydroxyl radicals, which enhanced the individual reaction steps in the SCR of NO_x . In our study, we propose that the oxygen

species over Ag/Al_2O_3 catalyst might be activated by the addition of H_2 , forming a peroxy-like species. This species appears to be highly active oxidant, and favorable to activate the C–C bond. We used H_2O_2 as a resource of active oxygen species and added it in a flow of $NO + C_3H_6 + O_2$. The result indicated that the SCR of NO_x by C_3H_6 was also promoted in the low temperature range from 423 K to 673 K (results not shown). Therefore, the peroxy-like species can oxidize C_3H_6 to more reactive oxygen-containing molecules as reaction intermediates at low temperatures.

In the case of $NO + C_3H_6 + O_2$ reaction without H_2 addition, the acetate species was negligible below 523 K, while the enolic species predominated on Ag/Al_2O_3 with H_2 addition (Fig. 4). As described above, the enolic species has higher activity than the acetate species towards nitrate to form $-NCO$ species, and the presence of H_2 enhances the enolic species formation within a wide temperature range during the SCR of NO_x . As a result, the $-NCO$ surface species with high concentration is formed under the presence of H_2 over a wide temperature region 523–673 K, which eventually results in a high NO_x conversion in the $NO + O_2 + C_3H_6 + H_2$ reaction over Ag/Al_2O_3 . In the absence of H_2 , the acetate, as a predominant product of partial oxidation, plays a key role in $-NCO$ formation. Its low reactivity results in a low concentration of $-NCO$ and a low NO_x conversion during the SCR of NO_x by C_3H_6 over a wide temperature region 523–673 K, as shown in Fig. 1.

GC–MS analyses also provide useful information about reaction pathway and intermediates during the SCR of NO_x by C_3H_6 . Oxygen-containing molecules have been proposed to be important intermediates. In comparison with Fig. 2A and B, it is evident that the presence of H_2 promotes the formation of oxygen-containing molecules (such as CH_3CHO and $CH_2=CHCHO$) and nitrogen-containing molecules (such as CH_3CN and CH_3NO_2) during the SCR of NO_x by C_3H_6 at 473 K, confirming that the addition of H_2 accelerates the reaction. As we proposed in our previous study, an enolic species structure $(RCH=CH-O^-)-M$ forms when CH_3CHO is adsorbed on the surface of Ag/Al_2O_3 . Therefore, the formation of enolic species could be attributed to the CH_3CHO tautomerization between the gaseous phase and catalyst surface. Shibata et al. [12] claimed that the addition of H_2 promoted the partial oxidation of C_3H_8 by surface nitrates to surface acetate, which was related to the rate-determining step of the SCR of NO_x by C_3H_8 in the absence of H_2 . We suggest



Scheme 1. The proposed main reaction pathway for the SCR of NO_x by C_3H_6 over Ag/Al_2O_3 in the presence of H_2 .

that the enhancement of H₂ on the NO_x reduction by C₃H₆ over Ag/Al₂O₃ at low temperatures is originated from an enhancement of H₂ on the partial oxidation of C₃H₆ to surface enolic species, which is more reactive than surface acetate species. Moreover, the transient DRIFTS experiments of reaction intermediates in Figs. 5 and 6 further confirmed that the reactivities of enolic species and –NCO species towards NO + O₂ were greatly enhanced by the addition of H₂.

On the basis of these results and discussions, we tentatively propose a main reaction pathway of the SCR of NO_x by C₃H₆ over Ag/Al₂O₃ in the presence of H₂, as shown in Scheme 1.

5. Conclusions

The activity of the SCR of NO_x by C₃H₆ over Ag/Al₂O₃ was significantly enhanced by the addition of H₂, especially in the low temperature range of 473–623 K. In situ DRIFTS spectra showed that the presence of H₂ promoted the formation of enolic species during the partial oxidation of C₃H₆ over Ag/Al₂O₃ catalyst. The presence of enolic species at low temperatures could provide insight into the high activity of NO_x reduction by C₃H₆ with H₂ as a co-reductant at low temperatures. GC–MS results also demonstrated such a H₂ promotional effect on the partial oxidation of C₃H₆ and the formation of nitrogen-containing products during the NO_x reduction by C₃H₆. In addition, the presence of H₂ further accelerated the reaction of enolic species and –NCO towards NO + O₂ to form N₂ as a final product.

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