Effect of hydrogen on reaction intermediates in the selective catalytic reduction of NO\textsubscript{x} by C\textsubscript{3}H\textsubscript{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\textsubscript{x} by C\textsubscript{3}H\textsubscript{6} in the presence of H\textsubscript{2} over Ag/Al\textsubscript{2}O\textsubscript{3} was investigated using in situ DRIFTS and GC–MS measurements. The addition of H\textsubscript{2} promoted the partial oxidation of C\textsubscript{3}H\textsubscript{6} to enolic species, the formation of –NCO and the reactions of enolic species and –NCO with NO\textsubscript{x} on Ag/Al\textsubscript{2}O\textsubscript{3} surface at low temperatures. Based on the results, we proposed reaction mechanism to explain the promotional effect of H\textsubscript{2} on the SCR of NO\textsubscript{x} by C\textsubscript{3}H\textsubscript{6} over Ag/Al\textsubscript{2}O\textsubscript{3} catalyst.

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1. Introduction

Emission control of NO\textsubscript{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\textsubscript{x} with various reductants has been extensively studied. Among a number of catalysts, alumina-supported silver (Ag/Al\textsubscript{2}O\textsubscript{3}) catalyst shows a very high activity for NO\textsubscript{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\textsubscript{x} by lower hydrocarbons, and this becomes a major disadvantage for practical use of this technology. A recent study found that addition of H\textsubscript{2} to feed stream could result in a remarkable improvement in the activity of NO\textsubscript{x} reduction and the active temperature range [6]. Furthermore, the positive effect of H\textsubscript{2} is found to be specific for silver catalysts such as Ag/Al\textsubscript{2}O\textsubscript{3} [6–8] and Ag-zeolites [9–11]. The effect of H\textsubscript{2} for the SCR of NO\textsubscript{x} over Ag/Al\textsubscript{2}O\textsubscript{3} catalyst has been investigated with several alkanes (e.g. propane, octane, decane). Using in situ FTIR spectroscopy, the promotional effect of H\textsubscript{2} on the oxidation of NO to NO\textsubscript{2} and the oxidation of hydrocarbons to acetates has been revealed on Ag/Al\textsubscript{2}O\textsubscript{3} [12–14]. Instead of NO oxidation, Shibata et al. [9–11] proposed that the positive effect of H\textsubscript{2} addition on the NO\textsubscript{x} reduction was attributed to the formation of small charged metallic Ag\textsuperscript{6+} clusters based on the results of UV–vis spectroscopy. Burch and Breen et al. [15,16] postulated that the improvement of added H\textsubscript{2} in the SCR of NO\textsubscript{x} was due to the formation of C=N species, and was not associated with significant structural changes in the Ag/Al\textsubscript{2}O\textsubscript{3} catalyst at low temperatures.

Based on our previous DRIFTS studies and DFT calculations, a novel mechanism of the SCR of NO\textsubscript{x} by C\textsubscript{2}H\textsubscript{5}OH or C\textsubscript{3}H\textsubscript{6} over Ag/Al\textsubscript{2}O\textsubscript{3} was proposed in the absence of H\textsubscript{2} [17,18]. As an important intermediate, an enolic species originated from partial oxidation of C\textsubscript{2}H\textsubscript{5}OH or C\textsubscript{3}H\textsubscript{6} was identified over Ag/Al\textsubscript{2}O\textsubscript{3}. The high surface concentration of enolic species is related with a high surface concentration of –NCO species and a high efficiency of NO\textsubscript{x} reduction by C\textsubscript{2}H\textsubscript{5}OH, whereas a low concentration of enolic species corresponds to a low efficiency for the NO\textsubscript{x} reduction by C\textsubscript{3}H\textsubscript{6} over Ag/Al\textsubscript{2}O\textsubscript{3}.

The promotional effect of H\textsubscript{2} on the formation of enolic species during the hydrocarbon oxidation on Ag/Al\textsubscript{2}O\textsubscript{3} catalyst has not been reported. This paper reports an effect of H\textsubscript{2} on the reduction of NO\textsubscript{x} by C\textsubscript{3}H\textsubscript{6} over Ag/Al\textsubscript{2}O\textsubscript{3} catalyst within low temperature region. The role of H\textsubscript{2} on the
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 cm⁻³ scm⁻¹, GHSV = ~50,000 h⁻¹). NOx conversion was analyzed on-line by a chemiluminescence NO/NO₂/NOx 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 × 0.32 mm, 20 μm 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 NOx by C₃H₆ over Ag/Al₂O₃

Fig. 1A shows the conversions of NOₓ for the C₃H₆-SCR with or without 1% H₂ over Ag/Al₂O₃ catalyst as a function of temperature. The NOₓ conversion in the absence of H₂ was less than 10% within the temperature range from 423 K to 573 K, and the maximum NOₓ conversion of 97% was achieved at 723 K. Clearly, the addition of H₂ significantly enhanced NOₓ conversion, especially in the temperature range of 473–623 K. The NOₓ 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 NOₓ 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 NOₓ 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
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 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...
attributed to $\nu_{as}$ (OCO) and $\nu_c$ (OCO) of adsorbed acetate, respectively \cite{3,4,21,22}, and the peaks at 1392 cm$^{-1}$ and 1377 cm$^{-1}$ are assigned to $\delta$ (–CH$_2$) and $\delta$ (–CH$_3$) of adsorbed acetate \cite{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 \cite{17,18}, the peak at 1633 cm$^{-1}$ could be assigned to $\nu_{as}$ (RCH–C–O) of a surface enolic species, which derived from the partial oxidation of C$_3$H$_6$. In the case of C$_3$H$_6$ + O$_2$, acetate was predominant species on the surface of Ag/Al$_2$O$_3$ within the whole temperature region. When H$_2$ was added to a flow of C$_3$H$_6$ + 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. 3A). This peak was accompanied by the appearance of strong bands at 1457 cm$^{-1}$ and 1336 cm$^{-1}$, which can be attributed to acetate. In addition, the peaks at 1411 cm$^{-1}$ for $\nu_{as}$ (RCH–C–O) and 1336 cm$^{-1}$ for $\delta$ (C–H) of the enolic species were also visible \cite{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$_3$H$_6$ at low temperatures. In the case of C$_3$H$_6$ + O$_2$ + 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 Ag/Al$_2$O$_3$ during the partial oxidation of C$_3$H$_6$ 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$_3$H$_6$ in the absence and presence of H$_2$ over Ag/Al$_2$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 Ag/Al$_2$O$_3$ surface by DRIFTS method. Fig. 4A and B show the in situ DRIFTS spectra of Ag/Al$_2$O$_3$ catalyst in a flow of NO + C$_3$H$_6$ + 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 NO + C$_3$H$_6$ + O$_2$ mixture gas at 423 K \cite{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 \cite{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 (1633 cm$^{-1}$) and the bidentate nitrates (1300 cm$^{-1}$) decreased gradually. Meanwhile, a weak band at 2230 cm$^{-1}$ assigned to isocyanate (–NCO) species appeared at 623 K \cite{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$_x$ to form –NCO \cite{18}. In the presence of H$_2$, the enolic species (1633 cm$^{-1}$) could be identified even at a 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$_3$H$_6$, and such facilitation was more significant at low temperatures. Compared with Fig. 4A, a new broad peak appeared around 1700–1750 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 Ag/Al$_2$O$_3$ surface, and the relation between the formation of –NCO species and consumption of enolic species became clear as shown in Fig. 4B. It is also noticeable that the appearance of –NCO peak at 2231 cm$^{-1}$ in Fig. 4B began at lower temperatures if comparing with the case of NO + C$_3$H$_6$ + O$_2$ in Fig. 4A, and the intensity of –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 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

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.
species almost disappeared. Moreover, the intensity of –NCO species also decreased. These results indicate that the presence of H₂ accelerates the reactions of enolic species and –NCO towards NO + O₂ to form N₂ as a final product.

4. Discussion

The reaction mechanism of the SCR of NOₓ by C₃H₆ over Ag/Al₂O₃ has been proposed and summarized as follows:

\[ \text{NO} + \text{O}_2 + \text{C}_3\text{H}_6 \rightarrow \text{NO}_2 \text{(nitrate in particular)} + \text{C}_3\text{H}_4\text{O} \text{(acetate in particular)} \rightarrow \text{R–ONO} + \text{R–NO}_2 \rightarrow \text{–NCO} + \text{–CN} + \text{NO} + \text{O}_2 \rightarrow \text{N}_2 + \text{CO}_3 \]

[4, 5, 21, 24–27]. Many research groups proposed that the acetate played a crucial role in the formation of –NCO species by reaction towards NO + O₂ at high temperatures. Recently, we found enolic species as an intermediate of partial oxidation of C₃H₂OH and C₃H₆ on Ag/Al₂O₃, and believed that the enolic species has much higher reactivity than acetate towards NO + O₂ 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 H₂ at a low temperature range (473–623 K). The oxidation of C₃H₆ was also promoted during the NO + C₃H₆ + O₂ reaction in the presence of H₂. There is a dramatic difference in the surface species concentration in the oxidation of C₃H₆ with and without H₂ (Fig. 3). The presence of H₂ clearly favors the partial oxidation and the formation of the enolic species over Ag/Al₂O₃. Recently, the formation and promotion of enolic species by adding H₂ were also observed in partial oxidation of other light hydrocarbons (results not shown). Hayashi et al. [28] reported that the oxidation of C₃H₆ was enhanced by H₂ over Au/TiO₂/SiO₂ catalyst. They suggested that dioxygen might be transformed by the reduction with H₂ to an active species over the catalyst, which had the ability to selectively oxidize C₃H₆ to propene oxide. The promotional effect of H₂ on the partial oxidation was also found by several other authors using different hydrocarbons as reducing agents in the SCR of NOₓ [8, 14, 15]. Richter et al. [8] speculated that molecular oxygen dissociates over small Ag⁰ clusters formed by hydrogen reduction of appropriately sized Ag₂O, and promotes oxidation of hydrocarbons to oxygenates. Sazama et al. [14] proposed that H₂ took part in the SCR of NOₓ by decane and reacted with oxygen to form hydroperoxy and hydroxyl radicals, which enhanced the individual reaction steps in the SCR of NOₓ. In our study, we propose that the oxygen species over Ag/Al₂O₃ catalyst might be activated by the addition of H₂, forming a peroxo-like species. This species appears to be highly active oxidant, and favorable to activate the C–C bond. We used H₂O₂ as a resource of active oxygen species and added it in a flow of NO + C₃H₆ + O₂. The result indicated that the SCR of NOₓ by C₃H₆ was also promoted in the low temperature range from 423 K to 673 K (results not shown). Therefore, the peroxo-like species can oxidize C₃H₆ to more reactive oxygen-containing molecules as reaction intermediates at low temperatures.

In the case of NO + C₃H₆ + O₂ reaction without H₂ addition, the acetate species was negligible below 523 K, while the enolic species predominated on Ag/Al₂O₃ with H₂ 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 H₂ enhances the enolic species formation within a wide temperature range during the SCR of NOₓ. As a result, the –NCO surface species with high concentration is formed under the presence of H₂ over a wide temperature region 523–673 K, which eventually results in a high NOₓ conversion in the NO + O₂ + C₃H₆ + H₂ reaction over Ag/Al₂O₃. In the absence of H₂, 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 NOₓ conversion during the SCR of NOₓ by C₃H₆ 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 NOₓ by C₃H₆. Oxygen-containing molecules have been proposed to be important intermediates. In comparison with Fig. 2A and B, it is evident that the presence of H₂ promotes the formation of oxygen-containing molecules (such as CH₃CHO and CH₂=CHCHO) and nitrogen-containing molecules (such as CH₃CN and CH₃NO₂) during the SCR of NOₓ by C₃H₆ at 473 K, confirming that the addition of H₂ accelerates the reaction. As we proposed in our previous study, an enolic species structure (RCH=CH–O–M) forms when CH₃CHO is adsorbed on the surface of Ag/Al₂O₃. Therefore, the formation of enolic species could be attributed to the CH₃CHO tautomerization between the gaseous phase and catalyst surface. Shibata et al. [12] claimed that the addition of H₂ promoted the partial oxidation of C₃H₆ by surface nitrates to surface acetate, which was related to the rate-determining step of the SCR of NOₓ by C₃H₆ in the absence of H₂. We suggest

Scheme 1. The proposed main reaction pathway for the SCR of NOₓ by C₃H₆ over Ag/Al₂O₃ in the presence of H₂.
that the enhancement of H2 on the NOx 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 NOx by C3H6 over Ag/Al2O3 in the presence of H2, as shown in Scheme 1.

5. Conclusions

The activity of the SCR of NOx 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 NOx 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 NOx 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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