A common feature of H_2-assisted HC-SCR over Ag/Al$_2$O$_3$†

Yunbo Yu, Hong He,* Xiuli Zhang and Hua Deng

CH_4, C_2H_2, C_2H_4, C_3H_6, and C_3H_8 were selected as reductants for selective catalytic reduction (SCR) of NO_x over Ag/Al$_2$O$_3$. Activity measurement showed that NO_x reduction by hydrocarbons containing two- or three-carbon atoms was clearly promoted by H_2 over Ag/Al$_2$O$_3$ at low temperatures, while such enhancement did not occur in the case of CH_4-SCR. Gas chromatography and gas chromatography coupled to a mass spectrometer analysis showed that the partial oxidation of hydrocarbons with more than one carbon atom was triggered at low temperatures by H_2 addition over Ag/Al$_2$O$_3$. On the surface of Ag/Al$_2$O$_3$, *in situ* diffuse reflectance infrared Fourier transform spectra indicated that this enhancement mainly originated from the formation of reactive enolic species, which is a common feature of H_2-assisted HC-SCR.

1. Introduction

Among the NO_x reduction technologies being developed for controlling diesel engine emissions, selective catalytic reduction by hydrocarbons (HC-SCR) has attracted much attention as a possible alternative to the commercially used NH$_3$/urea-SCR.[1–3] The distinctive advantage of HC-SCR is that the on-board fuel or additive can be used as the reductant for NO_x conversion, thus reducing the cost involved in the infrastructure development for reductant delivery. Hitherto, numerous catalysts such as zeolitic oxide, base oxide/metal and noble metal catalysts have been found to be effective for NO_x reduction by hydrocarbons, among which Ag/Al$_2$O$_3$ is known to be one of the most effective catalysts even in the presence of H_2O and SO_2.[1–6] More importantly, the low-temperature activity of Ag catalysts can be significantly boosted by H_2 addition both under laboratory conditions and in a full-scale vehicle equipped with a Ag/Al$_2$O$_3$ converter.[7,8]

To date, however, the origination of the H_2 effect is still under debate, and includes the formation of Ag clusters and their role in boosting HC-SCR, and chemical effects involving in reactive species contributing to NO_x reduction by hydrocarbons.[9–11] Using *in situ* ultraviolet-visible spectroscopy (UV-vis), extended x-ray absorption fine structure (EXAFS), and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) characterization, Satsuma and co-workers proposed

that hydrogen would be indispensable for the formation of Ag$_n^{\delta+}$ clusters, the presence of which is necessary for the promotion of C_3H_8 oxidation, and thus contributed to NO_x reduction over Ag catalysts.[11–13] The morphological transformation of Ag$^+$ to Ag$_n^{\delta+}$ was recently observed by Kim *et al.* during H_2 assisted C_2H_5OH + simulated diesel over Ag/Al$_2$O$_3$, in the case of which highly active oxygen species were created, enhancing the low-temperature deNO$_x$ activity of Ag/Al$_2$O$_3$.[14] On the other hand, the formation of oxidized Ag clusters was also identified by Burch and co-workers during C_8H_{18}-SCR in the presence of H_2 and CO over Ag/Al$_2$O$_3$, respectively, while CO did not boost the HC-SCR activity.[9,15,16] As a result, it was proposed that the promotion of H_2 in HC-SCR is not attributed to structural changes of the active sites but to a chemical effect, which was further announced by Sazama *et al.* and Korhonen *et al.*[17,18]

It has been generally accepted that the partial oxidation of hydrocarbons to active oxygenates, as an initial step of HC-SCR, was triggered by H_2 addition at low temperatures, and thus enhancing NO_x reduction.[11,12,19,20] By using *in situ* DRIFTS, Shibata *et al.* found that the addition of H_2 results in remarkable promotion of partial oxidation of C_3H_8 over Ag/Al$_2$O$_3$, mainly to surface acetate, which was later also reported by Bentrup and co-workers.[12,19] During the partial oxidation of C_3H_6 over Ag/Al$_2$O$_3$, however, He and co-workers proposed that the presence of H_2 promoted the formation of enolic species (RCH=CH–O$^-$)–M, particularly in the low temperature range.[20] The surface enolic species rather than acetate on Ag/Al$_2$O$_3$, exhibited higher activity toward NO + O_2 to produce the key intermediate of isocyanate (–NCO), and thus contributed to the promotion effect of H_2 on C_3H_6-SCR of NO_x. Previous research further established that enolic species play a key role in the reduction of NO_x by alcohols (such as ethanol

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and butanol) over Ag/Al_2O_3,[14,21–23] acetaldehyde over both Ag/Al_2O_3 and Co/Al_2O_3,[24,25] and acetylene over ZSM-5.[26] Interestingly, Taatjes and co-workers also observed substantial quantities of two-, three-, and four-carbon enols using photoionization mass spectrometry (PIMS) of flames burning representative compounds from modern fuel blends, indicating that enols are common intermediates in hydrocarbon oxidation.[27] Herein, CH_4, C_2H_2, C_2H_4, C_3H_6, and C_3H_8 were selected as reductants for NO_x reduction over Ag/Al_2O_3. It was found that the formation of enolic species was triggered by H_2 addition during the oxidation of all the employed hydrocarbons containing two or three carbons at low temperatures, which may reveal the intrinsic mechanism contributing to H_2 assisted HC-SCR over Ag/Al_2O_3.

2. Experimental

2.1. Catalyst preparation and characterization

As described in our earlier papers, the Ag/Al_2O_3 catalyst with a silver loading of 4 wt% was prepared by an impregnation method, immersing boehmite into an aqueous solution of silver nitrate.[2,23] After impregnation, the excess water was removed using a rotary evaporator at 333 K and then the sample was calcined in air at 873 K for 3 h. The catalyst prepared by this method exhibited a specific surface area of 239.8 m^2 g^{-1}. UV-vis analysis showed that Ag species were mainly present in the oxidized state (Ag^+ and $Ag_n^{\delta+}$ clusters), particularly as highly dispersed Ag^+ ions, which was in agreement with the results of XRD and TEM characterization.[23]

2.2. Activity tests

The inlet and outlet concentrations of hydrocarbons during their oxidation over Ag/Al_2O_3 were analyzed by gas chromatography (Agilent 6890N GC) equipped with Porapak Q column. During this process, the products were also measured by gas chromatography (Agilent 6890N GC) coupled to a mass spectrometer (Agilent 5973N MS) with a column-containing HP–PLOT Q (Agilent 30 m × 0.32 mm, 20 μm film). The typical experiment conditions were as follows: 2571 ppm CH_4 (or 2571 ppm C_2H_2, or 2571 ppm C_2H_4, or 1714 ppm C_3H_6, or 1714 ppm C_3H_8), 800 ppm NO (if used), 10% O_2, and N_2 as balance. The total gas flow rate was 2000 mL min^{-1} over 0.6 g catalyst (W/F = 0.018 g s mL, GHSV = 50 000 h^{-1}). NO_x conversion was analyzed on-line by a chemiluminescence $NO/NO_2/NO_x$ analyzer (42C–HL, Thermo Environmental Instrument Inc.).

2.3. In situ DRIFTS study

In situ DRIFTS spectra were recorded on a Nexus 670 FT-IR (Thermo Nicolet), equipped with an *in situ* diffuse reflection chamber and a high sensitivity MCT/A detector. In this case, Ag/Al_2O_3 catalyst was finely ground and placed in ceramic crucibles in the *in situ* chamber. Mass flow controllers and a sample temperature controller were used to simulate the real reaction conditions, such as mixture of gases, pressure and sample temperature. Prior to recording each DRIFTS spectrum,

the sample was heated *in situ* in 10% O_2/N_2 flow at 823 K for 1 h, then cooled to the desired temperature to measure a reference spectrum. All gas mixtures were fed at a flow rate of 300 mL min^{-1}. All spectra were measured with a resolution of 4 cm^{-1} and with an accumulation of 100 scans.

3. Results

3.1. Activity tests with or without H_2

We conducted a comparative study of the effect of H_2 on the oxidization of CH_4, C_2H_2, C_2H_4, C_3H_6, and C_3H_8 over Ag/Al_2O_3 catalyst, respectively (Fig. 1A). It was evident that the addition of 1% H_2 promoted the catalytic oxidation of hydrocarbons having more than one carbon atom in the temperature region of 423–773 K, while only a marginal effect was observed during CH_4 oxidation.

The products in the gas phase during the oxidation of different hydrocarbons containing least two carbon atoms over Ag/Al_2O_3 were further measured by GC-MS. As for C_2H_2 oxidation (Fig. S1A and B†), a certain amount of acetaldehyde (CH_3CHO) and acetone (CH_3COCH_3) were observed both in the presence and in the absence of H_2 at temperatures below 673 K, together with the formation of CO_2, CO, and H_2O. This result indicates that partial oxidation occurred over Ag/Al_2O_3. During the oxidation of C_2H_4 over Ag/Al_2O_3 (Fig. S1C and D†), the final products of CO_2, CO, and H_2O were also detected, while the partial oxidation products mentioned above were hardly observed in the gas phase even in the presence of H_2. At temperatures above 673 K, acetone was measured during the oxidation of C_3H_6 and C_3H_8 over Ag/Al_2O_3 (Fig. S1E and G†); after H_2 was co-fed (Fig. S1F and H†), this species was observed within the whole temperature range, together with the formation of acetaldehyde at low temperatures. These results clearly suggest that H_2 promotes partial oxidation of hydrocarbons, in particular for C_3H_6 and C_3H_8.

The presence of H_2 significantly promoted NO_x reduction by hydrocarbons containing at least two carbon atoms over Ag/Al_2O_3, while it hardly changed the NO_x conversion by CH_4 (Fig. 1B). Among the employed hydrocarbons, C_3H_6 was the most active for NO_x reduction in the presence of H_2, exhibiting 90% NO_x conversion even at a temperature as low as 490 K. The most significant promotion effect of H_2 was observed during the C_3H_8-SCR process, giving a T_{50} for NO_x conversion (temperature for 50% NO_x conversion) of 479 K, 205 K lower than that in the absence of H_2 (Table 1). Within the whole temperature region, NO_x conversion by CH_4 was lower than 15%, indicating that the C1 reductant was not active for the SCR of NO_x over Ag/Al_2O_3.

3.2. In situ DRIFTS studies

To identify the origin of the H_2 effect on the surface species formed by oxidation of the different hydrocarbons, *in situ* DRIFTS studies were performed (Fig. 2, see also Fig. S2†). For CH_4 oxidation over Ag/Al_2O_3, peaks at 1595 and 1392 cm^{-1} were observed, which were due to ν_{as} (OCO) and ν_s (OCO) of formate, respectively.[17] By comparison with their intensity,
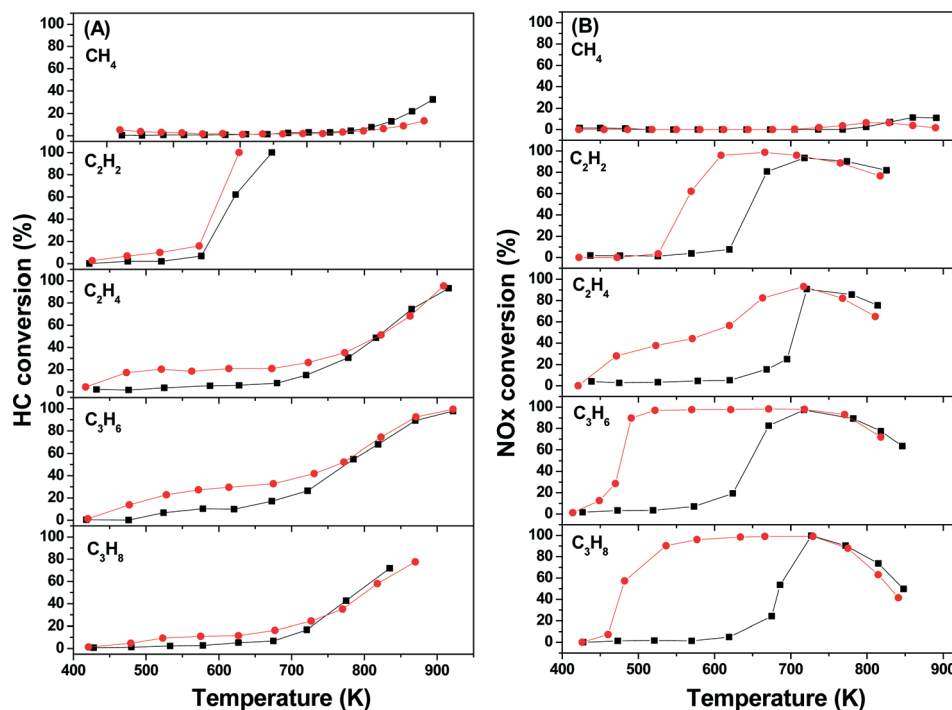
Fig. 1 (A) Conversion of hydrocarbons over Ag/Al$_2$O$_3$ during hydrocarbon oxidation with 1% H$_2$ (●) and without H$_2$ (■). (B) NO$_x$ conversion during HC-SCR over Ag/Al$_2$O$_3$. Feed: 2571 ppm CH$_4$ (or 2571 ppm C$_2$H$_2$, or 2571 ppm C$_2$H$_4$, or 1714 ppm C$_3$H$_6$, or 1714 ppm C$_3$H$_8$), 800 ppm NO (if used), 10% O$_2$, N$_2$ balance, total flow rate = 2000 mL min^{-1}, GHSV = 50 000 h^{-1}.

it indicates that the formation of formate was hardly changed upon H$_2$ addition within the temperature range of 473–773 K (Fig. S2A and B†). The peaks at 1550 and 1460 cm^{-1} can be assigned to surface carbonates (Fig. S2A and B†).[28] In the presence of H$_2$, the peak at 1651 cm^{-1} assignable to adsorbed water was observed at 473 K, the appearance of which was detected over Ag/Al$_2$O$_3$ in flowing H$_2$ + O$_2$ at temperatures between 423–523 K (Fig. S2K†).

During the oxidation of C$_2$H$_2$ over Ag/Al$_2$O$_3$ (Fig. 2, see also Fig. S2C and D†), surface formate was also observed at temperatures below 723 K. Meanwhile, the appearance of peaks at 1573 and 1464 cm^{-1} indicates the formation of surface acetate.[12,17,29,30] The peaks at 1633, 1415, and 1336 cm^{-1} can be assigned to surface enolic species.[14,21–25] Introduction of H$_2$ into the feed gas changes the intensity of peaks due to the acetate and enolic species. Particularly at low temperatures, H$_2$ promotes the formation of surface enolic species over Ag/Al$_2$O$_3$.

The peak at 1676 cm^{-1} can be assigned to the stretching vibration model of C=O in acetone adsorbed on the surface,[31] the formation of which in the gas phase has been confirmed by GC-MS analysis.

Formate, acetate, and enolic species also formed during catalytic oxidation of C$_2$H$_4$, C$_3$H$_6$, and C$_3$H$_8$ over Ag/Al$_2$O$_3$ (Fig. 2, see also S2E–J†). For C$_2$H$_4$ and C$_3$H$_8$ oxidation, it should be noted that surface acetate was more pronounced than enolic species in the presence of H$_2$ within temperatures range of 523–773 K. During the oxidation of C$_3$H$_6$ over Ag/Al$_2$O$_3$, the promotion effect of H$_2$ on the formation of enolic species was more significant than that of C$_2$H$_4$. In the former case, the peak at 1633 cm^{-1} due to enolic species exhibits the strongest intensity within the temperature range of 473–523 K, indicating a high concentration on the surface of Ag/Al$_2$O$_3$.

To clearly illustrate the changes in surface enolic species and acetate triggered by the addition of H$_2$ during the oxidation

Table 1 Temperature required for the formation of surface enolic species (1633 cm^{-1}) and acetate (1464 cm^{-1}) with the strongest intensity (T_{max}) during hydrocarbon oxidation and temperature required for 50% NO$_x$ conversion (T_{50}) during HC-SCR over Ag/Al$_2$O$_3$

| | T_{max} for enolic species formation (K) | | | T_{max} for acetate formation (K) | | | T_{50} for NO$_x$ conversion (K) | | |
	Without H$_2$	With H$_2$	ΔT_{max}[a]	Without H$_2$	With H$_2$	ΔT_{max}[b]	Without H$_2$	With H$_2$	ΔT_{50}[c]
C$_2$H$_2$	623	573	50	673	623	50	649	560	89
C$_2$H$_4$	673	523	150	773	673	100	705	594	111
C$_3$H$_6$	723	523	200	773	573	200	647	477	170
C$_3$H$_8$	773	523	250	773	573	200	684	479	205

[a] ΔT_{max} = T_{max} for enolic species formation without H$_2$ − T_{max} for enolic species formation with H$_2$. [b] ΔT_{max} = T_{max} for acetate formation without H$_2$ − T_{max} for acetate formation with H$_2$. [c] ΔT_{50} = T_{50} for NO$_x$ conversion without H$_2$ − T_{50} for NO$_x$ conversion with H$_2$.

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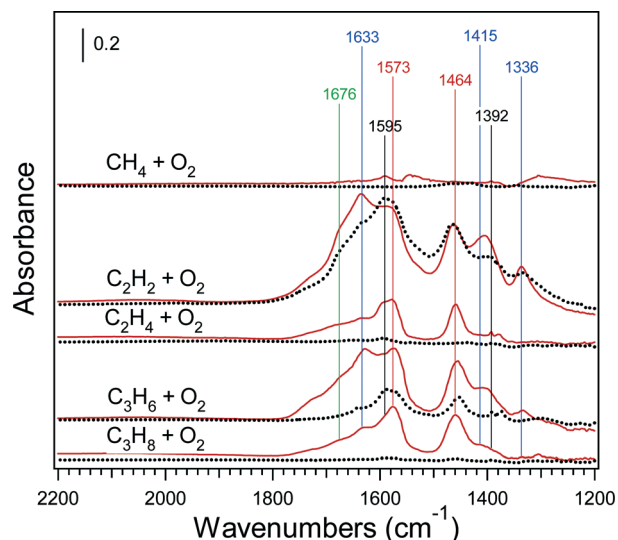**Fig. 2** *In situ* DRIFTS spectra of Ag/Al$_2$O$_3$ at steady state at 523 K during oxidation of hydrocarbons without H$_2$ (dotted line) and with H$_2$ (solid line). The components of the feed gas are the same as in Fig. 1, while total flow rate = 300 mL min^{-1}.

of hydrocarbons, the spectra (Fig. S2C–J†) in the range of 1200–2000 cm^{-1} were converted into Kubelka–Munk functions,[32] and then fitted on the basis of the deconvoluted curves

(typical results for the deconvolution and curve fitting were presented in Fig. S3†). After Kubelka–Munk conversion, the integrated areas of peaks at 1633 (for enolic species) and 1464 cm^{-1} (for acetate) in Fig. S2C–J† are displayed as a function of temperature (Fig. 3). Based on these, one can obtain the temperature at which the enolic species and acetate exhibit the strongest intensity (hereafter denoted as T_{max}, see also Table 1) during the oxidation of hydrocarbons. Then, the change of T_{max} for the two surface species originating from H$_2$ addition can be calculated, as shown in Table 1 (hereafter denoted as ΔT_{max}). Taking C$_2$H$_2$ oxidation as a example, H$_2$ addition promoted the formation of enolic species at low temperatures, exhibiting the maximum area at the temperature of 573 K (T_{max} = 573 K), 50 K lower than that in the absence of H$_2$ (ΔT_{max} = 50 K).

During the oxidation of C$_2$H$_2$, C$_2$H$_4$, C$_3$H$_6$, and C$_3$H$_8$ in the presence of H$_2$, it should be noted that the T_{max} values for enolic species were always lower than those for acetate. These results indicate that the stability of enolic species is lower than acetate, providing the opportunity to react with N-containing species at low temperatures.[8–11] Meanwhile, different hydrocarbons exhibit different T_{max} values for the formation of enolic species; for a given hydrocarbon, the value of T_{max} is dramatically changed by the addition of H$_2$. As a result, the T_{max} value for the enolic species formation and its change by H$_2$ addition reveal key clues that predict the
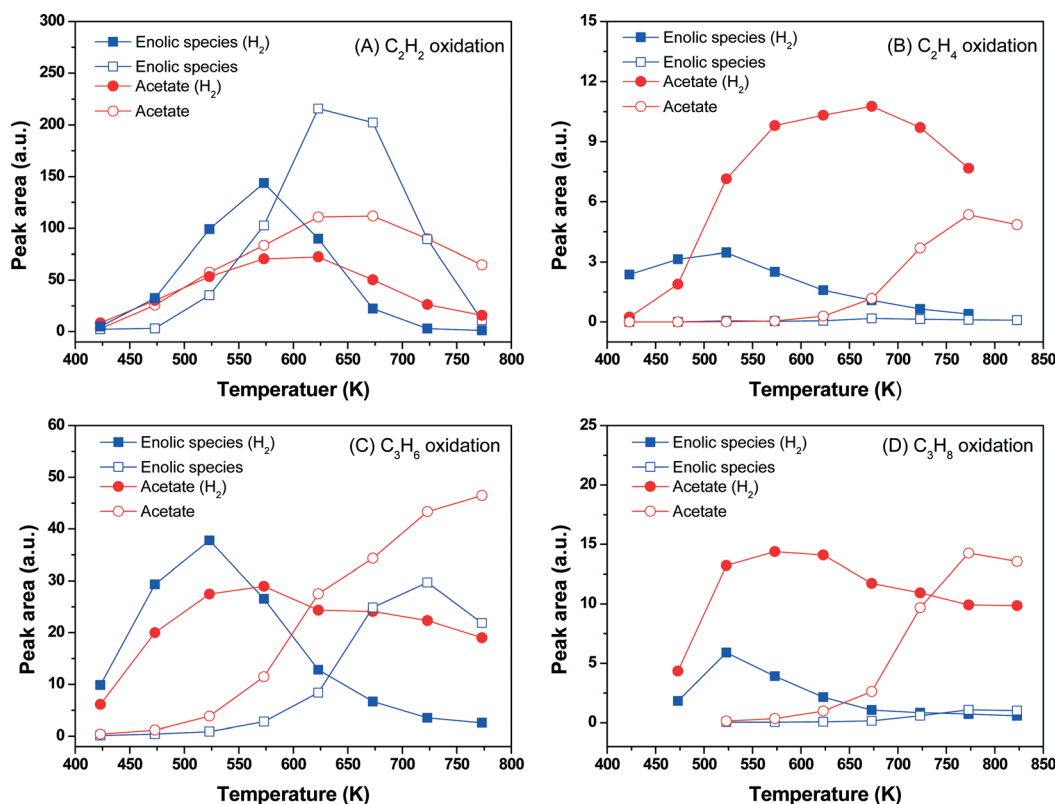

Fig. 3 The integrated areas of the peaks due to enolic species (1633 cm^{-1}) and acetate (1464 cm^{-1}) during the oxidation of C$_2$H$_2$ (A), C$_2$H$_4$ (B), C$_3$H$_6$ (C), and C$_3$H$_8$ (D) at different temperatures.

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intrinsic properties during hydrocarbon oxidation, and also for HC-SCR over Ag/Al_2O_3. Indeed, the T_{max} for enolic species commonly appeared at the light-off temperature range for NO_x reduction in the presence of H_2 (usually denoted as T_{50}, see also Table 1), possibly indicating their key role in H_2-assisted HC-SCR. To further elucidate this association, the relationship between the ΔT_{max} for enolic species and corresponding change of T_{50} for NO_x conversion (ΔT_{50}) during HC-SCR is shown graphically in Fig. 4. The stronger the promotion effect of H_2 on the formation of enolic species, the more significant the enhancement of H_2 on NO_x conversion is, confirming the crucial role of enolic species in H_2-assisted HC-SCR. Interestingly, the peaks herein assigned to enolic species were also observed by other researchers during C_3H_6-SCR and C_8H_{18}-SCR, particularly in the presence of H_2 over Ag/Al_2O_3, although they had been considered to represent surface acrylate species.[33–35]

In situ DRIFTS studies were also performed during the NO_x reduction by different hydrocarbons (Fig. 5, see also Fig. S4, ESI†). Similarly, H_2 promoted the partial oxidation of C_2H_2, C_2H_4, C_3H_6, and C_3H_8 to produce enolic species (1633 and 1336 cm^{-1}) and acetate (1573 and 1464 cm^{-1}) over Ag/Al_2O_3. In contrast, both species were absent in the NO_x reduction by CH_4, leaving large amounts of nitrates on the surface of Ag/Al_2O_3, exhibiting the feature frequencies of 1550 and 1251 cm^{-1} for monodentate nitrate, 1589 and 1306 cm^{-1} for bidentate nitrate, and 1612 cm^{-1} for bridging nitrate.[17,36] Taking the activity results into account (Fig. 1B), it may be the case that a hydrocarbon containing at least two carbon atoms is required for NO_x reduction with high efficiency, even in the presence of H_2. The peak for –NCO, as a key intermediate in HC-SCR over Ag/Al_2O_3, was observed at 2235 cm^{-1}, the intensity of which was enhanced by H_2 addition during NO_x reduction by C_2H_4, C_3H_6, and C_3H_8.[1–3,34,37] As for C_2H_2-SCR, however, a much stronger intensity –NCO peak was observed in the absence of H_2, indicating that only a fraction of all the –NCO observed by DRIFTS is reactive and able to serve as a potential intermediate for NO_x reduction at a given temperature.[35]

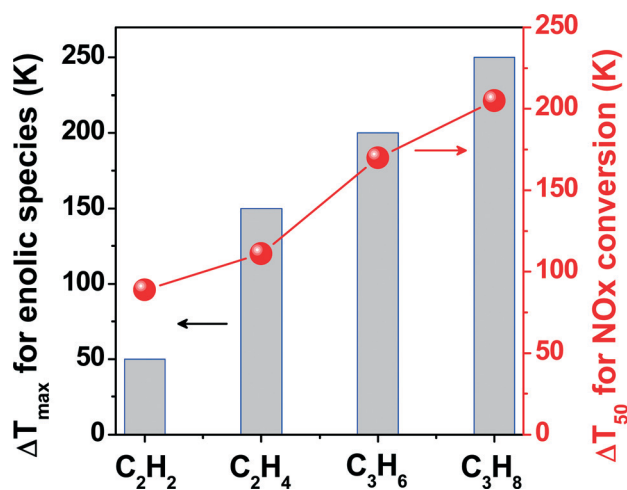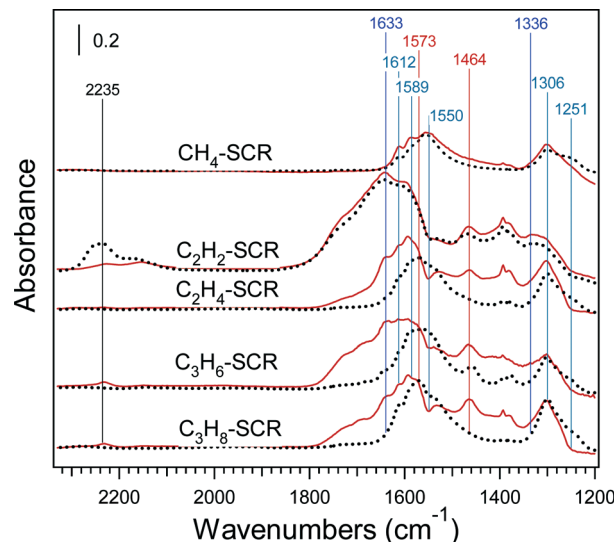**Fig. 5** *In situ* DRIFTS spectra of Ag/Al_2O_3 at steady state at 523 K during the NO_x reduction by different hydrocarbons without H_2 (dotted line) and with H_2 (solid line).

4. Discussion

Previous studies, mainly achieved by *in situ* DRIFTS, confirmed that surface enolic species originating from the partial oxidation of ethanol gave high activity for reaction with $NO + O_2$ to produce N_2 *via* the formation of organo-nitrogen compounds, which can be considered as follows: $NO + O_2 + C_2H_5OH \rightarrow$ ad-NO_x + enolic species (acetate also formed) $\rightarrow$ R–ONO + R–NO_2 $\rightarrow$ –NCO + –CN $\rightarrow$ N_2.[20–23] By using PIMS analysis, ethenol in the gas phase as an important intermediate during the catalytic oxidation of ethanol over Ag/Al_2O_3 catalyst was unambiguously identified,[38,39] further confirming the formation of surface enolic species during the NO_x reduction by ethanol over Ag/Al_2O_3. Acetate was also formed during partial oxidation of ethanol, while it exhibits lower concentration and low activity toward $NO + O_2$ than enolic species, resulting in a minor role in ethanol-SCR over Ag/Al_2O_3.

As for partial oxidation of C_2H_4, C_3H_6, and C_3H_8 in the absence of H_2 over Ag/Al_2O_3 (Fig. 2 and 3), acetate was the main product. As a result, it is reasonable that these reductants are not active for NO_x reduction in the absence of H_2, particularly at low temperatures (Fig. 1). It should be noted that H_2 promoted the formation of enolic species during the partial oxidation of C_2H_2, C_2H_4, C_3H_6, and C_3H_8 over Ag/Al_2O_3, particularly in the low temperature range of 423–523 K (Fig. 2 and 3). The stronger the promotion of enolic species formation, the higher the activity for NO_x reduction (Fig. 4). As suggested by GC-MS measurement, acetaldehyde was often produced during partial oxidation of hydrocarbons described above. Previous studies have confirmed that the adsorption of acetaldehyde on the surface of Ag catalyst induced the formation of enolic species.[21,24] As a result, it is reasonable that a higher concentration of enolic species was observed on the surface of the catalyst, and meanwhile, acetaldehyde was unambiguously detected in the gas phase (Fig. S1† and 2).

Fig. 4 Relationship between the ΔT_{max} for enolic species triggered by H_2 addition and ΔT_{50} for NO_x conversion during HC-SCR.

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Based on these findings, a universal pathway of H_2-promoted HC-SCR over Ag/Al$_2$O$_3$ was proposed, as shown in Fig. 6. The employed hydrocarbons containing at least two carbon atoms is necessary for the formation of active enolic species during their partial oxidation over Ag/Al$_2$O$_3$, and was significantly enhanced by H_2 addition. In this case, the formation of enolic species and its further reaction to produce N_2 is the main pathway for NO_x reduction with high efficiency in the presence of H_2. In our previous research,[22] it was also proposed that oxygenated hydrocarbons such as alcohols containing at least one C–C bond are prerequisite for enolic species formation during their partial oxidation over Ag/Al$_2$O$_3$. This intrinsic property has been further clarified during partial oxidation of CH_3OH, in which the enolic species was rarely observed over Ag/Al$_2$O$_3$.[40,41] A similar result was also observed in flowing $CH_4 + O_2$ over Ag/Al$_2$O$_3$. Thus, the pathway of CH_4-SCR even in the presence of H_2 is quite different to the others presented here.

Sazama and Wichterlová found that the presence of hydrogen peroxide enhanced substantially the activity of Ag/Al$_2$O$_3$ for NO_x reduction by decane.[9] By using ESR measurements, Shimizu *et al.* provided evidence for the *in situ* generation of superoxide ions (O_2^-) in $H_2 + O_2$ and H_2-assisted C_3H_8-SCR reactions over Ag/Al$_2$O$_3$.[13] This active oxygen species enhanced partial oxidation of hydrocarbon to acetate, thus contributing to the "H_2 effect". More recently, Shimizu *et al.* also proposed that the presence of H_2 promoted activation of O_2 to OOH species over Ag-MFI, the occurrence of which is crucial for the partial oxidation of C_3H_8.[11] In our case, it is possible that the reactive oxygen species mentioned above would be produced in the presence of H_2, and then trigger the formation of enolic species during partial oxidation of hydrocarbons having more than one carbon atom over Ag/Al$_2$O$_3$.

It has been widely accepted that the structure of hydrocarbons has a great influence on the activity of Ag/Al$_2$O$_3$ for NO_x reduction.[1,4] As for NO reduction by various alkanes over Ag catalysts, Satsuma and co-workers found that both the reaction rates of NO and hydrocarbons had good correlations with the mean bond energy of the alkanes, which is an average of all C–H and C–C bond energies in the hydrocarbons.[4,42] Further research achieved by *in situ* DRIFTS experiments revealed that these correlations could be rationalized by the reaction rate of the formation of surface oxygenated species such as acetate, which was significantly promoted by the presence of H_2.[4,12] In our case, the intrinsic properties of the employed hydrocarbons, such as carbon number, C–H and C–C bond energies, the adsorption enthalpy of hydrocarbons,

and so on, may contribute to the formation of enolic species, and to the promotion of H_2 on enolic species formation.

5. Conclusions

NO_x reduction by hydrocarbons containing two- or three-carbon atoms was clearly promoted by H_2 at low temperatures, while this promotion effect of H_2 did not occur during the CH_4-SCR over Ag/Al$_2$O$_3$. *In situ* DRIFTS spectra identified that the formation of enolic species was triggered by H_2 addition during the oxidation of the hydrocarbons containing two or three carbons at low temperatures, while the enolic species was hardly observed during CH_4 oxidation. The stronger the promotion effect of H_2 on enolic species formation, the more significant the enhancement of NO_x conversion, confirming the crucial role of enolic species in H_2-assisted HC-SCR, and thus creating an effective pathway for NO_x reduction.

Acknowledgements

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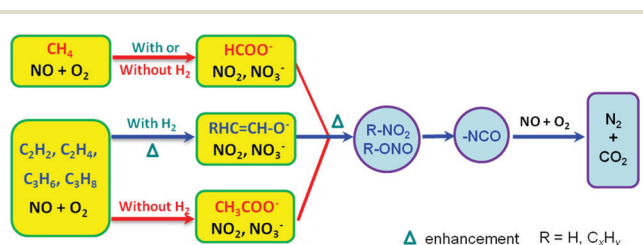
Fig. 6 Proposed mechanism of H_2-assisted HC-SCR over Ag/Al$_2$O$_3$.

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