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A common feature of H₂-assisted HC–SCR over Ag/Al₂O₃

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CH₄, C₂H₂, C₂H₄, C₃H₆, and C₃H₈ were selected as reductants for selective catalytic reduction (SCR) of NOx over Ag/Al₂O₃. Activity measurement showed that NOx reduction by hydrocarbons containing two- or three- carbon atoms was clearly promoted by H₂ over Ag/Al₂O₃ at low temperatures, while such enhancement did not occur in the case of CH₄-SCR. Gas chromatography and gas chromatography coupled to a mass spectrometer analysis showed that the partial oxidation of hydrocarbons having more than one carbon atom was triggered at low temperatures by H₂ addition over Ag/Al₂O₃. On the surface of Ag/Al₂O₃, 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 H₂-assisted HC-SCR.

1. Introduction

Among the NOx reduction technologies being developed for controlling diesel engine emission, selective catalytic reduction by hydrocarbons (HC–SCR) has attracted much attention as a possible alternative to the commercially used NH₃/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 NOx 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 NOx reduction by hydrocarbons, among which Ag/Al₂O₃ is known as one of the most effective catalysts even in the presence of H₂O and SO₂.¹⁻⁶ More importantly, the low-temperature activity of Ag catalysts can be significantly boosted by H₂ addition both under laboratory conditions and on a full-scale vehicle equipped with a Ag/Al₂O₃ converter.⁷⁻⁸

Up to date, however, the origination of the H₂ effect is still under debate, including the formation of Ag clusters and their role in boosting HC-SCR, and chemical effect involving in reactive species contributed to NOx 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 NOx reduction over Ag catalysts.¹¹⁻¹³ The morphological transformation of Ag^+ to $Ag_n^{\delta^+}$ was recently observed by Kim et al. during H₂ assisted C₂H₅OH + simulated diesel over Ag/Al₂O₃, in the case of that highly active oxygen species was created, enhancing the low-temperature deNOx activity of Ag/Al₂O₃.¹⁴ 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/Al₂O₃,

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 H₂ addition at low temperatures, and thus enhancing NOx reduction.^{11,12,19,20} By using in situ DRIFTS, Shibata et al. found that the addition of H₂ results in remarkable promotion of partial oxidation of C₃H₈ over Ag/Al₂O₃, mainly to surface acetate, which was later also reported by Bentrup and co-workers.^{12,19} During the partial oxidation of C₃H₆ over Ag/Al₂O₃, however, He and co-workers proposed that the presence of H₂ 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/Al₂O₃, exhibited higher activity toward NO + O_2 to produce the key intermediate of isocyanate (-NCO), and thus contributed to the promotion effect of H2 on C3H6-SCR of NOx. Previous research further established that enolic species play a key role in the reduction of NOx by alcohols (such as ethanol 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, CH₄, C₂H₂, C₂H₄, C₃H₆, and C₃H₈ were selected as reductants for NOx reduction over Ag/Al2O3, respectively. It was found that the formation of enolic species was triggered by H₂ 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 H₂ assisted HC-SCR over Ag/Al₂O₃.

2. Experimental

2.1. Catalyst preparation and characterization

As described in our earlier papers, Ag/Al₂O₃ catalyst with silver loading of 4wt% was prepared by an impregnation method, immersing boehmite into an aqueous solution of silver nitrate.² After impregnation, the excess water was removed in 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 m²/g. UV-vis analysis showed that Ag species were mainly present in the oxidized state (Ag⁺ and Ag_n^{δ +} 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/Al₂O₃ 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 CH₄ (or 2571 ppm C₂H₂, or 2571 ppm C₂H₄, or 1714 ppm C₃H₆, 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 over 0.6 g catalyst (W/F = 0.018 g s mL, 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. 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/Al₂O₃ 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% O₂/N₂ 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 H₂

We conducted a comparative study of the effect of H₂ on the oxidization of CH₄, C₂H₂, C₂H₄, C₃H₆, and C₃H₈ over Ag/Al₂O₃ catalyst, respectively (Fig. 1A). It was evident that the addition of 1% H₂ 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 CH₄ oxidation.



Fig. 1. (A) Conversion of hydrocarbons over Ag/Al_2O_3 during hydrocarbon oxidation with 1% $H_2(\bullet)$ and without $H_2(\bullet)$. (B) NOx conversion during HC-SCR over Ag/Al₂O₃. Feed: 2571 ppm CH₄ (or 2571 ppm C₂H₂, or 2571 ppm C₂H₄, or 1714 ppm C₃H₆, or 1714 ppm C₃H₈), 800 ppm NO (if used), 10% O₂, N₂ balance, total flow rate = 2000 mL/min, GHSV=50,000 h^{-1}

The products in gas phase during the oxidation of different hydrocarbons containing least two carbon atoms over Ag/Al₂O₃ were further measured by GC-MS. As for C₂H₂ oxidation (Fig. S1A and S1B), certain amount of acetaldehyde (CH₃CHO) and acetone (CH₃COCH₃) were observed both in the presence and in the absence of H₂ at temperatures below 673 K, together with the formation of CO₂, CO, and H₂O. This result indicates that partial oxidation was occurred over Ag/Al₂O₃. During the oxidation of C₂H₄ over Journal Name

Ag/Al₂O₃ (Fig. S1C and S1D), the final products of CO₂, CO, and H₂O were also detected, while the partial oxidation products mentioned above were hardly observed in the gas phase even in the presence of H₂. At temperatures above 673 K, acetone was measured during the oxidation of C₃H₆ and C₃H₈ over Ag/Al₂O₃ (Fig. S1E and S1G); after H₂ was co-fed (Fig. S1F and S1H), this species was observed within the whole temperature range, together with the formation of acetaldehyde at low temperatures. These results clearly suggest that H₂ promotes partial oxidation of hydrocarbons, in particular for C₃H₆ and C₃H₈.

The presence of H₂ significantly promoted NOx reduction by hydrocarbons containing at least two carbon atoms over

Ag/Al₂O₃, while it hardly changed the NOx conversion by CH₄ (Fig. 1B). Among the employed hydrocarbons, C₃H₆ was the most active for NOx reduction in the presence of H₂, exhibiting 90% NOx conversion even at a temperature as low as 490 K. The most significant promotion effect of H₂ was observed during the C₃H₈–SCR process, giving a T_{50} for NOx conversion (temperature for 50% NOx conversion) of 480 K, 205 K lower than that in the absence of H₂ (Table 1). Within the whole temperature region, NOx conversion by CH₄ was lower than 15%, indicating that the C1 reductant was not active for the SCR of NOx over Ag/Al₂O₃.

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% NOx conversion (T_{50}) during HC–SCR over Ag/Al₂O₃.

	T _{max} for enolic species formation (K)			T _{max} for acetate formation (K)			T ₅₀ for NOx conversion (K)		
	Without	With H ₂	ΔT_{max}^{a}	Without	With H ₂	ΔT_{max}^{b}	Without	With H ₂	ΔT_{50}^{c}
	H_2			H_2			H_2		
C_2H_2	623	573	50	673	623	50	649	560	89
C_2H_4	673	523	150	773	673	100	705	594	111
C_3H_6	723	523	200	773	573	200	647	477	170
C_3H_8	773	523	250	773	573	200	684	479	205
C ₃ H ₈	//3	523	250	//3	5/3	200	684	4/9	205

 $^{a}\Delta T_{max} = T_{max}$ for enolic species formation without H₂ - T_{max} for enolic species formation with H₂;

^b $\Delta T_{max} = T_{max}$ for acetate formation without H₂ – T_{max} for acetate formation with H₂;

^c $\Delta T_{50} = T_{50}$ for NOx conversion without $H_2 - T_{50}$ for NOx conversion with H_2 .

3.2. In situ DRIFTS studies

To identify the origination of the H₂ effect on the surface species formed by oxidation of the different hydrocarbons, *in situ* DRIFTS studies were performed (Fig. 2, see also Fig. S2). As for CH₄ oxidation over Ag/Al₂O₃, the peaks at 1595 and 1392 cm⁻¹ were observed which were due to v_{as} (OCO) and v_s (OCO) of formate, respectively.¹⁷ By comparison with their intensity, it indicates that the formation of formate was hardly changed by H₂ addition within the temperature of 473–773 K (Fig. S2A and S2B). The peaks at 1550 and 1460 cm⁻¹ can be assigned to surface carbonates (Fig. S2A and S2B).²⁸ In the presence of H₂, the peak at 1651 cm⁻¹ assignable to adsorbed water was observed at 473 K, the appearance of which was detected over Ag/Al₂O₃ in flowing H₂ + O₂ at temperatures between 423–523 K (Fig. S2K).

During the oxidation of C_2H_2 over Ag/Al_2O_3 (Fig. 2, see also Fig. S2C and S2D), 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 H₂ into the fed gas changes the intensity of peaks due to the acetate and enolic species. Particularly at low temperatures, H₂ promotes the formation of surface enolic species over Ag/Al₂O₃. 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 C_2H_4 , C_3H_6 , and C_3H_8 over Ag/Al₂O₃ (Fig. 2, see also Fig. S2E-S2J). As for C_2H_4 and C_3H_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_3H_6 over Ag/Al₂O₃, the promotion effect of H_2 on the formation of enolic species was

more significant than that of C_2H_4 . In the former case, the peak at 1633 cm⁻¹ due to enolic species exhibits the strongest intensity within the temperature between 473–523 K, indicating a high concentration on the surface of Ag/Al₂O₃.



Fig. 2. In situ DRIFTS spectra of Ag/Al_2O_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 at total flow rate = 300 mL/min.

To clearly illustrate the changes of surface enolic species and acetate triggered by the addition of H₂ during the oxidation of hydrocarbons, the spectra (Fig. S2C–2J) in the range of 1200–2000 cm⁻¹ were converted into Kubelka–Munk function,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–S2J 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 H₂ addition can be calculated, as shown in Table 1 (hereafter denoted as ΔT_{max}). Taking C₂H₂ oxidation as a example, H₂ 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 H₂ (ΔT_{max} = 50 K).



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_2H_2 (A), C_2H_4 (B), C_3H_6 (C), and C_3H_8 (D) at different temperatures, respectively.

During the oxidation of C_2H_2 , C_2H_4 , C_3H_6 , and C_3H_8 in the presence of H₂, 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 H₂ addition reveal key clues that predict the intrinsic properties during hydrocarbon oxidation, and also for HC-SCR over Ag/Al₂O₃. Indeed, the T_{max} for enolic species commonly appeared at the light-off temperature range for NOx reduction in the presence of H₂ (usually denoted as T₅₀, see also Table 1), possibly indicating their key role in H2-assisted HC-SCR. To further elucidate this association, the relationship between the ΔT_{max} for enolic species and corresponding change of T₅₀ for NOx 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 H₂ on NOx conversion is, confirming the crucial role of enolic species in H₂-assisted HC-SCR. Interestingly, the peaks herein assigned to enolic species were also observed by other researchers during C₃H₆-SCR and C₈H₁₈-SCR, particularly in

the presence of H_2 over Ag/Al₂O₃, although they had been considered to represent surface acrylate species.³³⁻³⁵



Fig. 4. Relationship between the ΔT_{max} for enolic species triggered by H₂ addition and ΔT_{50} for NOx conversion during HC–SCR.

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The in situ DRIFTS studies were also performed during the NOx reduction by different hydrocarbons (Fig. 5, see also Fig. S4 and ESI). Similarly, H₂ promoted the partial oxidation of C₂H₂, C₂H₄, C₃H₆, and C₃H₈ to produce enolic species (1633 and 1336 cm⁻¹) and acetate (1573 and 1464 cm⁻¹) over Ag/Al_2O_3 . In contrast, both the species were absent in the NOx reduction by CH₄, leaving large amounts of nitrates on the surface of Ag/Al₂O₃, 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 NOx reduction with high efficiency, even in the presence of H₂. The peak for -NCO, as a key intermediate in HC-SCR over Ag/Al₂O₃, was observed at 2235 cm⁻¹, the intensity of which was enhanced by H_2 addition during NOx 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 NOx 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 NOx reduction by different hydrocarbons without H₂ (dotted line) and with H₂ (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 + O₂ to produce N₂ via the formation of organo-nitrogen compounds, which can be considered as follows: NO + O₂ + C₂H₅OH \rightarrow ad-NOx + enolic species (acetate also formed) \rightarrow R–ONO + R– NO₂ \rightarrow –NCO + –CN \rightarrow N₂.²⁰⁻²³ By using PIMS analysis, ethenol in gas phase as an important intermediate during the catalytic oxidation of ethanol over Ag/Al₂O₃ catalyst was unambiguously identified,^{38,39} further confirming the formation of surface enolic species during the NOx reduction by ethanol over Ag/Al₂O₃. Acetate was also formed during partial oxidation of ethanol, while it exhibits lower concentration and low activity toward NO + O₂ than enolic species, resulting in a minor role in ethanol-SCR over Ag/Al₂O₃.

As for partial oxidation of C₂H₄, C₃H₆, and C₃H₈ in the absence of H₂ over Ag/Al₂O₃ (Figs. 2 and 3), acetate was the mainly product. As a result, it is reasonable that these reductants are not active for NOx reduction in the absence of H₂ particularly at low temperatures (Fig. 1). It should be noted that, H₂ promoted the formation of enolic species during the partial oxidation of C₂H₂, C₂H₄, C₃H₆, and C₃H₈ over Ag/Al₂O₃, particularly in the low temperature range of 423–523 K (Figs. 2 and 3). The stronger the promotion of enolic species formation, the higher the activity for NOx reduction is (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 during acetaldehyde was unambiguously detected in the gas phase (Fig. S1 and Fig. 2).



Fig. 6. Proposed mechanism of H₂-assisted HC–SCR over Ag/Al₂O₃.

Based on these findings, a universal pathway of H2promoted HC-SCR over Ag/Al₂O₃ 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/Al₂O₃, which was significantly enhanced by H₂ addition. In this case, the formation of enolic species and its further reaction to produce N₂ is the main pathway for NOx reduction with high efficiency in the presence of H_2 . In our previous research,²² it was also proposed that the oxygenated hydrocarbon such as alcohols containing at least one C-C bond is prerequisite for enolic species formation during their partial oxidation over Ag/Al₂O₃. This intrinsic property has been further clarified during partial oxidation of CH₃OH, in which the enolic species was rarely observed over Ag/Al₂O₃.^{40,41} Similarly result was also observed in flowing CH₄ + O₂ over Ag/Al₂O₃. Thus, the pathway of CH₄-SCR even in the presence of H₂ is quite different with others presented here.

Sazama and Wichterlová found that the presence of hydrogen peroxide enhanced substantially the activity of Ag/Al_2O_3 for NOx reduction by decane.⁹ By using ESR measurement, 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_2O_3 .¹³ This active oxygen species enhanced partial oxidation of hydrocarbon to acetate, thus contributing to the "H₂ 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 reactive oxygen species mentioned above would be produced in the presence of H_2 , and then triggered the formation of enolic species during partial oxidation of hydrocarbons having more than one carbon atom over Ag/Al_2O_3 .

It has been widely accepted that the structure of hydrocarbons has a great influence on the activity of Ag/Al₂O₃ for NOx 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 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 H₂.^{4,12} In our cases, 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 contributed to the formation of enolic species, and to the promotion of H_2 on enolic species formation.

5. Conclusions

NOx reduction by hydrocarbons containing two- or threecarbon 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/Al₂O₃. 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 NOx conversion is, confirming the crucial role of enolic species in H_2 -assisted HC-SCR, and thus creating an effective pathway for NOx reduction.

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Notes and references

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- † Electronic Supplementary Information (ESI) available: details of GC-MS analysis, and DRIFTS studies. See DOI: 10.1039/b000000x/
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Table of contents entry

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