

Precipitable silver compound catalysts for the selective catalytic reduction of NO_x by ethanol

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ABSTRACT

The Ag/Al₂O₃, Ag₃PO₄/Al₂O₃, Ag₂SO₄/Al₂O₃ and AgCl/Al₂O₃ catalysts showed high activities for the selective catalytic reduction (SCR) of NO_x by ethanol. AgCl was highly crystalline on Al₂O₃, however, AgCl/Al₂O₃ gave the highest catalytic turnover frequency (TOF) for NO_x reduction among the four catalysts. Calculated Mulliken charges of Ag compounds support the TOF results. The activity test and characterization results confirm that Ag⁺ is the active silver species for NO_x reduction. The in situ FT-IR results of Ag₃PO₄/Al₂O₃, Ag₂SO₄/Al₂O₃ and AgCl/Al₂O₃ for NO_x reduction further reveal a positive correlation between the high dispersion of Ag⁺ and the formation of active intermediates (the enolic and –NCO species), indicating a similar reaction pathway to that of the ethanol-SCR over Ag/Al₂O₃. Using the precipitable silver compounds greatly facilitates the preparation of monolith Ag/Al₂O₃ catalyst for practical usage. In fact, the high performance of the AgCl/Al₂O₃ honeycomb catalyst was confirmed by heavy duty diesel engine bench tests.

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1. Introduction

The selective catalytic reduction of NO_x by hydrocarbons (HC-SCR) is a potential method to remove NO_x from oxygen rich exhausts of automobiles and stationary facilities. Ag/Al₂O₃ is known to be one of the most effective catalysts for the SCR of NO_x by hydrocarbons. So far, catalytic performance, catalyst characterization and reaction mechanism of the HC-SCR of NO_x over Ag/Al₂O₃ have been investigated in detail by many researchers, as well as applications on the de-NO_x of diesel engine exhaust [1–15]. Since the catalytic performance of Ag/Al₂O₃ has a close relationship with Ag loading and the Ag physical and chemical states, the structures of the Ag species as active sites on Al₂O₃ have attracted much attention [4,9,11,16,17]. It is accepted that silver oxide species with high dispersion are observed with lower Ag loading, and their presence is related to their high NO_x reduction performance [2,9,16,18,19]. On the contrary, a higher percentage of metal loading correlates with the formation of metallic Ag on the catalyst surface, which favors oxidation of the reductant by O₂ and decreases its selectivity for NO_x reduction [4,9,16,19]. Usually, the highest HC-SCR activity can be observed at low or moderate Ag loadings (2–4 wt.%). Miyadera [2] proposed that oxidized Ag

species interacting with the alumina support were the active phase for the HC-SCR reactions. Hoost et al. [10] pointed out that metal–support interaction might be associated with high de-NO_x efficiency on the optimum 2 wt.% Ag/Al₂O₃. Bethke and Kung [4] reported that 2 wt.% Ag/Al₂O₃ contained Ag in the +1 oxidation state, which resulted in a high NO_x conversion, while the 6 wt.% Ag/Al₂O₃ contained Ag⁰ particles, which resulted in a high rate of C₃H₆ combustion at the expense of NO_x reduction. Shimizu et al. [9] have reported that highly dispersed Ag⁺ ions are the dominant Ag species in the case of 2 wt.% Ag loading or below, and are responsible for the selective reduction of NO to N₂ over Ag/Al₂O₃ by higher hydrocarbons. These reports strongly suggest that the oxidation state of Ag on Ag/Al₂O₃ catalyst is very important for the de-NO_x performance, even though the active Ag phase might have different structures, such as isolated Ag⁺ ions, Ag_n^{δ+} clusters, silver oxide and silver aluminate.

Various methods have been used to obtain a catalyst containing the +1 state of Ag, including choosing different preparation methods and supports. It is known that impregnation of the alumina supports with a silver salt solution can lead to a wide distribution of Ag species according to the loading and kind of alumina used. The sol–gel [9,20], multiple impregnation [10], co-precipitation [20] and inverse micro-emulsion [21] methods were used to prepare the catalysts to obtain a greater dispersion of the metal cations or to promote strong interactions with the alumina support. Dilute nitric acid leaching has been used to remove Ag

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particles and all weakly bound Ag from the surface of Ag/Al₂O₃ [22].

In the previous studies [2,6,23], ethanol was shown to be extremely effective for NO_x reduction over Ag/Al₂O₃ in the presence of H₂O and SO₂. As for the reaction mechanism of the SCR of NO_x by ethanol, we have attributed the excellent performance for the SCR of NO_x by ethanol to the formation of enolic species on Ag/Al₂O₃ [24,25]. The adsorbed enolic species is more active to react with NO + O₂ on Ag/Al₂O₃ than acetate, and plays a crucial role in the formation of –NCO which is a key intermediate during the SCR of NO_x. However, the relationship between the active Ag site structure and the SCR activity has not been reported in detail. Moreover, eluted Ag⁺ ions from Ag/Al₂O₃ were found in the water [26]. The release of the Ag⁺ ions resulted in a re-distribution of Ag species during the preparation of Ag/Al₂O₃ washcoated cordierite honeycomb catalysts, further influencing the stability of the catalysts for NO_x reduction. In fact, precipitable silver compounds can be used to stabilize and control the state of the Ag phase. However, little research involving this aspect has been conducted [11,27–29].

The aim of the present work is to investigate the fixation and stabilization of Ag species on Al₂O₃, and to develop a better understanding of the active nature of Ag/Al₂O₃ for NO_x reduction by ethanol. For this purpose, AgNO₃ was used as the Ag precursor, while (NH₄)₃PO₄, (NH₄)₂SO₄ and NH₄Cl were used to precipitate silver compounds on Al₂O₃. The catalysts were characterized by N₂ adsorption, X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) measurements. The dispersion of the Ag species was measured by H₂–O₂ titration, and the turnover frequency (TOF) of NO_x conversion was calculated to compare the activities of silver oxide, AgCl, Ag₃PO₄ and Ag₂SO₄. The in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was used to investigate the intermediates interacting with the active Ag sites during NO_x reduction.

2. Experimental

2.1. Catalyst preparation

2.1.1. Preparation of powder catalysts

The AlOOH powder (surface area = 292.1 m² g⁻¹), used as Al₂O₃ precursor, was impregnated with an appropriate amount of silver nitrate aqueous solution to obtain a suspension. Subsequently, an appropriate amount of ammonium phosphate, ammonium sulfate or ammonium chloride was added dropwise to the suspension. The suspension was then dried at 393 K overnight and calcined at 873 K for 3 h in air to obtain the Ag/Al₂O₃, Ag₃PO₄/Al₂O₃, Ag₂SO₄/Al₂O₃ or AgCl/Al₂O₃ catalysts. Ag₃PO₄, Ag₂SO₄ and AgCl should not be decomposed at 873 K. In all cases, Ag loading of these catalysts was 4 wt.%.

2.1.2. Preparation of washcoated honeycomb catalysts

Washcoated honeycomb catalysts were prepared using the Ag₃PO₄/Al₂O₃ and AgCl/Al₂O₃ powder catalysts. Washcoat slurries were prepared by mixing 250 g of powder with 750 g of water using a ball mill. Cordierite honeycombs with 400 cells per square inch (90 mm in diameter × 110 mm in length) were dipped into the washcoat slurry, and excess slurry was blown out with an air jet. The samples were then dried at 393 K overnight and calcined at 873 K for 3 h. The washcoat loading was 110 g L⁻¹ after calcination.

2.2. Catalyst activity test

The measurement of the catalytic activity of Ag/Al₂O₃, Ag₃PO₄/Al₂O₃, Ag₂SO₄/Al₂O₃ and AgCl/Al₂O₃ powder catalysts was carried out in a fixed-bed reactor connected with a temperature controller.

The typical experiment conditions were as follows. The feed gas stream consisted of 800 ppm NO, 1565 ppm C₂H₅OH, 10% O₂ and 10% H₂O with N₂ as the balance. The total gas flow rate was 2000 cm³ min⁻¹ over 0.6 g catalyst (about 2.4 ml). W/F = 0.018 g s cm⁻³, gas hourly space velocity (GHSV) = ~50,000 h⁻¹. The NO_x conversion was analyzed on-line by a chemiluminescence NO/NO₂/NO_x analyzer (42C-HL, Thermo Environmental Instruments Inc.). Meanwhile, the concentration of N₂O during the NO_x reduction was measured on-line by an Agilent 6890N GC equipped with a Porapak Q column and a TCD detector (Agilent Technologies). In addition, the formation of organo-nitrogen compounds was also detected by GC–MS (Agilent GC (6890N)–MS (5973N), Agilent Technologies). Thus, N₂ concentration was calculated assuming that there was a mass balance of 100% for all the nitrogen-containing molecules [8,16,17].

The Ag₃PO₄/Al₂O₃ and AgCl/Al₂O₃ washcoat honeycomb catalysts were cut into small pieces (about 1.2 cm in diameter, 2.2 cm in length, and 2.5 cm³ in volume), and the measurements of the catalytic activity were carried out in the fixed-bed reactor. The feed gas stream consisted of 800 ppm NO, 1565 ppm C₂H₅OH, 10% O₂ and 10% H₂O with N₂ as the balance (GHSV = 50,000 h⁻¹, W/F = 0.008 g s cm⁻³).

The AgCl/Al₂O₃ washcoated honeycomb catalyst was used in the diesel engine bench tests (GHSV = ~30,000 h⁻¹); the NO_x conversion was measured with a gas analyzer (CEB-2, AVL). The engine used in this experiment was a Sofim 8140-43C diesel engine (four-cylinder direct injection, displacement 2.8 L, compression ratio 18.5:1, rated power/speed 76 kW/3600 rpm) as described in the previous work [30,31]. A portion of the exhaust gas was extracted and passed through a particulate trap. The catalysts were exposed to the exhaust with C₂H₅OH injection in front of the catalyst. The tests were conducted under the following conditions: engine speed 3450 rpm, torque 195 N m (full load), original NO_x emission 6.924 g kW⁻¹ h⁻¹ (around 500 ppm), C₂H₅OH/NO_x = 3:1 on a mass ratio.

2.3. Catalyst characterization

The nitrogen adsorption–desorption isotherms were obtained at 77 K over the whole range of relative pressures, using a Quantasorb-18 (Quanta Chrome Instrument Co.). Specific areas were computed from these isotherms by applying the Brunauer–Emmett–Teller (BET) method.

The samples were characterized by XRD using a computerized Rigaku D/max-RB Diffractometer (Japan, Cu Kα radiation, 0.154056 nm). Scans were taken over a 2θ range of 10–90° at a speed of 4° min⁻¹.

The catalysts were analyzed using XPS to identify the surface nature and concentration of the active species. Spectra were recorded by an ESCALAB Mark II spectrometer (Thermo ESCALAB 250, USA) using Al Kα radiation (hν = 1486.6 eV).

2.4. TOF study

Ag dispersions for Ag/Al₂O₃, Ag₃PO₄/Al₂O₃, Ag₂SO₄/Al₂O₃ and AgCl/Al₂O₃ were measured using H₂–O₂ titration [10], which was performed on a fixed-bed flow reactor system equipped with a computer-interfaced quadruple mass spectrometer (Hiden HPR 20). In order to remove the surface contaminants such as water and carbonates species, the catalyst sample was pretreated in 20% O₂ at 773 K for 30 min. After cooling to room temperature in the same atmosphere, the catalyst was reduced in a flow of H₂/Ar (5%) for 2 h at 523 K (raised at a ramp of 10 K min⁻¹), and cooled to 443 K (the temperature of O₂ adsorption) in the same atmosphere. Then the sample was purged with 30 cm³ min⁻¹ He stream for 30 min, and O₂ adsorption took place in a flow of 20% O₂ for 90 min (for Ag₃PO₄/

Al₂O₃, Ag₂SO₄/Al₂O₃, AgCl/Al₂O₃) or 30 min (for Ag/Al₂O₃) at the same temperature (443 K). After a second purge by 30 cm³ min⁻¹ He for 30 min, the adsorbed oxygen was titrated using H₂/Ar (5%), and the amount of hydrogen consumed was determined by a mass spectrometer. We selected the reduction temperature at 523 K (raised at a ramp of 10 K min⁻¹) and the reduction pretreatment of 2 h to ensure that the degree of reduction in these conditions was approximately 100%.

The Ag dispersion was calculated on the total adsorption stoichiometric ratio of Ag/O₂ = 2 and Ag/H₂ = 1 [10]. In this paper, the Ag dispersion and TOF for the NO_x reduction over the Ag species are expressed using Eqs. (1) and (2):

$$\text{Ag dispersion (\%)} = \frac{n_{\text{Ag}}(\text{calculation}) (\text{mol})}{n_{\text{Ag}} (\text{mol})} \times 100 \quad (1)$$

$$\text{TOF (s}^{-1}\text{)} = \frac{\text{NOx conversion (mol s}^{-1}\text{)}}{n_{\text{Ag}} (\text{mol}) \times \text{Ag dispersion}} \quad (2)$$

where $n_{\text{Ag}}(\text{calculation})$ is the calculated mole number of the surface Ag from H₂-O₂ titration, and n_{Ag} is the total mole number of 4 wt.% Ag loaded on the alumina support. Based on the Ag dispersion and NO_x conversion at 523 K, the TOFs for Ag/Al₂O₃, Ag₃PO₄/Al₂O₃, Ag₂SO₄/Al₂O₃ and AgCl/Al₂O₃ catalysts were calculated using Eq. (2).

2.5. In situ DRIFTS study

In situ DRIFTS experiments were performed on a Nexus 670 (Thermo Nicolet) FT-IR spectrometer equipped with an in situ diffuse reflection chamber and a high-sensitivity MCT detector. In these studies, the Ag/Al₂O₃, Ag₃PO₄/Al₂O₃, Ag₂SO₄/Al₂O₃ or AgCl/Al₂O₃ was finely ground and placed in a ceramic crucible in the in situ chamber. Mass flow controllers and a sample temperature controller were used to simulate the real reaction conditions, which were the same as those in the catalytic activity tests. Prior to recording each DRIFTS spectrum, the Ag/Al₂O₃ catalyst was heated in situ in a flow of 10% O₂/N₂ at 873 K for 1 h and then cooled to the desired temperature to acquire a reference spectrum. All spectra reported here were collected with a resolution of 4 cm⁻¹ for 100 scans.

3. Theoretical

The density functional theory (DFT) calculations were carried out using the Gaussian 98 program. The Mulliken charges of AgCl, Ag₂SO₄, Ag₃PO₄ and Ag₂O were calculated using the B3PW91 gradient corrected function (Becke's 3 parameter function with the non-local correlation provided by the Perdew 91 expression). The 3-21G basis set was used for all calculations.

4. Results and discussion

4.1. Activity tests

Fig. 1 shows the reaction activities of various silver compound catalysts supported on Al₂O₃ for the SCR of NO_x by ethanol. In all cases, the reaction began at 423 K and the NO_x conversion to N₂ was enhanced by the increase of temperature, with the maximum NO_x conversion to N₂ as high as 99% at 673 K. It is worth noting that no significant differences in activity were observed among the Ag/Al₂O₃, Ag₃PO₄/Al₂O₃ and Ag₂SO₄/Al₂O₃ catalysts over the whole temperature range. Compared to the other three catalysts, the AgCl/Al₂O₃ catalyst gave a 50% NO_x conversion to N₂ at a slightly higher temperature. Considering that the oxidation state of the Ag in Ag₃PO₄/Al₂O₃, Ag₂SO₄/Al₂O₃ and AgCl/Al₂O₃ is +1 throughout,

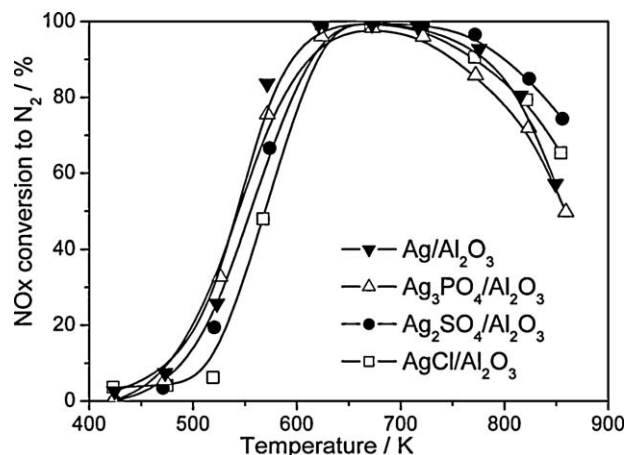


Fig. 1. NO_x conversion to N₂ for the SCR of NO_x by C₂H₅OH over various Al₂O₃-supported Ag compound catalysts. Conditions: 800 ppm NO, 1565 ppm C₂H₅OH, 10% H₂O, 10% O₂ in N₂ balance at a total flow rate of 2000 cm³ min⁻¹, W/F = 0.018 g s cm⁻³, GHSV = ~50,000 h⁻¹.

we suppose that the silver in the +1 oxidation state (Ag(I)) might be the active site of Ag/Al₂O₃. N₂O, the main nitrogen-containing by-product during NO_x reduction, was also measured on-line. In all cases, only trace amount of N₂O was measured in the whole temperature range, lower than 10 ppm. In addition, the formation of organo-nitrogen compounds was detected by GC-MS. Only trace amount of CH₃NO₂ was observed at 473 and 523 K, while trace amount of CH₃CN was observed at 573 and 623 K. The organo-nitrogen products were not quantified but this was thought to affect the N balance to only a minor extent [8,16].

4.2. Catalyst characterization

In order to investigate the relationship between the activity and the Ag state in these catalysts, we performed XRD and BET measurements on various silver catalysts supported on Al₂O₃. The structures of the catalysts are revealed by XRD, as shown in Fig. 2. Labels are used to indicate the crystalline structures which exist in each sample. The diffraction peaks observed at $2\theta = 37.0^\circ$, 45.9° , and 66.8° are all attributed to crystallized γ -Al₂O₃ (PDF-ICDD, 77-0396). No diffraction lines attributable to crystals of metallic Ag, AgOx, Ag₃PO₄ or Ag₂SO₄ were observed in the cases of Ag/Al₂O₃, Ag₃PO₄/Al₂O₃, and Ag₂SO₄/Al₂O₃ catalysts. It should be noted that

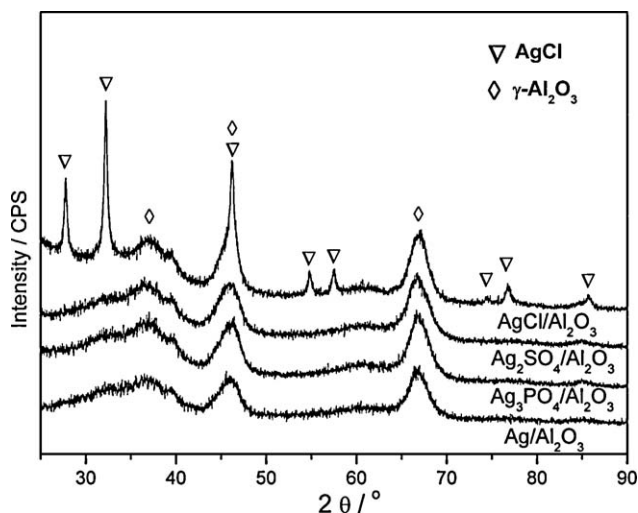
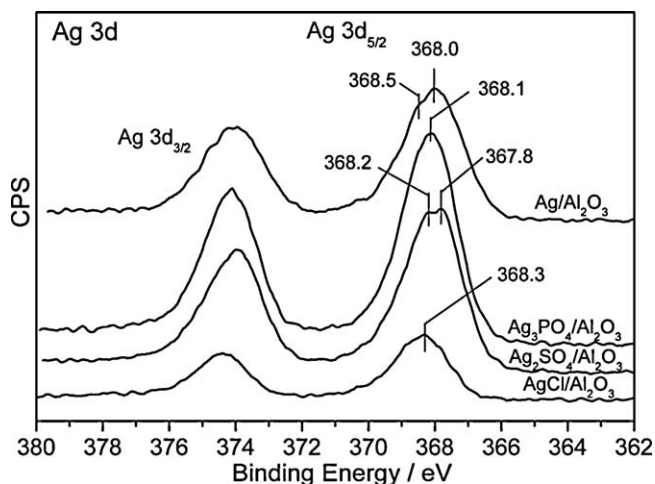


Fig. 2. XRD patterns of the various silver compound catalysts supported on Al₂O₃.

Table 1The surface areas, the Ag dispersions, the TOFs, and the Mulliken charges of the various silver compound catalysts supported on Al₂O₃.

Catalysts	Ag/Al ₂ O ₃	Ag ₃ PO ₄ /Al ₂ O ₃	Ag ₂ SO ₄ /Al ₂ O ₃	AgCl/Al ₂ O ₃
Surface area (m ² g ⁻¹)	254.8	255.1	238.0	224.9
Ag dispersion (%)	12.6	6.1	5.2	0.6
NOx conversion (%; 523 K)	26	33	19	6
TOF (10 ⁻² s ⁻¹) for NOx reduction	1.1	2.9	2.0	6.0
Mulliken charges of Ag in silver compounds ^a	0.215 ^a	0.378 ^b	0.421 ^c	0.503 ^d

^a The average Mulliken charges of Ag in Ag₂O^a, Ag₃PO₄^b, Ag₂SO₄^c, and AgCl^d.**Fig. 3.** High-resolution XPS spectra of the Ag 3d level for the various silver compound catalysts supported on Al₂O₃.

the Ag₃PO₄/Al₂O₃ catalyst shows a faint yellow color after calcination at 873 K, indicating the presence of Ag₃PO₄. Considering that AgCl, Ag₃PO₄ and Ag₂SO₄ could not have been decomposed at the calcination temperature (873 K), it is obvious that Ag, Ag₃PO₄ and Ag₂SO₄ are highly dispersed on the γ-Al₂O₃ [27–29]. However, the obvious XRD peaks attributable to crystallized AgCl were observed at 2θ = 32.2° for the AgCl/Al₂O₃ catalyst [27], which indicates the lower dispersion of Ag(I) in comparison with the other three catalysts. The BET surface areas of the catalysts are presented in Table 1. It is obvious that Ag/Al₂O₃ and Ag₃PO₄/Al₂O₃ have similar surface areas, followed by Ag₂SO₄/Al₂O₃, while AgCl/Al₂O₃ has the smallest surface area. The lower dispersion of AgCl on Al₂O₃ and lower surface area could account for the slight decrease of the apparent activity for NOx reduction over AgCl/Al₂O₃ in the temperature range 473–623 K (Fig. 1).

Table 1 also shows the Ag dispersions of the four catalysts and their TOFs for NOx reduction at 523 K. The Ag dispersions and the TOFs were calculated based on formulae (1) and (2) shown in Section 2, respectively. It is clear that the dispersion of Ag on the surface follows the order of Ag/Al₂O₃ > Ag₃PO₄/Al₂O₃ > Ag₂SO₄/

Al₂O₃ > AgCl/Al₂O₃. The lowest Ag dispersion (for the AgCl/Al₂O₃ catalyst) is in agreement with the XRD result of AgCl/Al₂O₃. The order of TOFs is AgCl/Al₂O₃ >> Ag₃PO₄/Al₂O₃ > Ag₂SO₄/Al₂O₃ > Ag/Al₂O₃. In particular, the TOF of AgCl/Al₂O₃ for NOx reduction is 5 times higher than Ag/Al₂O₃, while Ag₃PO₄/Al₂O₃ and Ag₂SO₄/Al₂O₃ give similar values, also twice higher than Ag/Al₂O₃. These results indicate that the anions associated with the silver ion have a significant positive influence on the SCR of NOx by C₂H₅OH, which may be owing to the high polarity of AgCl, Ag₃PO₄ and Ag₂SO₄ and finally relative to a strong stabilization of Ag(I) [32]. To clarify this hypothesis, we calculated the Mulliken charges of Ag in Ag₂O, Ag₃PO₄, Ag₂SO₄ and AgCl based on DFT theory; the results are shown in Table 1. Obviously, the average Mulliken charges of Ag in the four silver compounds follow the same order of TOFs for NOx reduction: AgCl (0.503) > Ag₂SO₄ (0.421) ≈ Ag₃PO₄ (0.378) > Ag₂O (0.215), exactly interpreting the positive effects of anions on the intrinsic activities of the four catalysts. That is, chloride gives much stronger electron withdrawing ability to keep the highly positive charge on Ag in AgCl, which is more favorable for stabilizing the oxidation of Ag and obtaining a high TOF for AgCl/Al₂O₃.

The Ag valence state of the supported Ag was further characterized by high-resolution XPS, with the results shown in Fig. 3 and summarized in Table 2. As can be seen in Fig. 3, the peaks of the Ag3d_{5/2} binding energy for all samples appeared at around 367.8–368.3 eV. As reported by Hammond et al. [33], Ag is unusual in that its core-level photoemissions shift to lower binding energy with increasing oxidation state. The binding energies of Ag3d_{5/2} in Ag/Al₂O₃, Ag₃PO₄/Al₂O₃, Ag₂SO₄/Al₂O₃ and AgCl/Al₂O₃ are 368.0, 368.1, 368.2 and 368.3 eV, respectively, which are consistent with the binding energies of Ag3d_{5/2} in Ag₂O, Ag₃PO₄, Ag₂SO₄ and AgCl according to the literature values of 367.9 eV [34], 368.2 eV [35], 368.3 eV [36] and 368.1 eV [37]. In addition, a shoulder at 368.5 eV for Ag/Al₂O₃ might be attributed to Ag⁰ (Ag3d_{5/2} = 368.4 eV) [38] on the surface. As for Ag₂SO₄/Al₂O₃, another peak of Ag3d_{5/2} is present at 367.8 eV, indicating that some of the loaded Ag in Ag₂SO₄/Al₂O₃ could exist in the form of Ag₂O (Ag3d_{5/2} = 367.9 eV) [34]. In addition, the apparent surface Ag content was estimated from the integrated peak area of Ag3d_{5/2} relative to that of all elements on each catalyst, as shown in Table 2. The order of apparent surface Ag content (Ag at.%) for the four catalysts is as follows: Ag₃PO₄/Al₂O₃ > Ag₂SO₄/Al₂O₃ > Ag/Al₂O₃ > AgCl/Al₂O₃.

Table 2

Characteristics of the Ag species in the silver compound catalysts as analyzed with XPS.

Catalysts	Binding energy (eV)		Apparent surface Ag content (at.%) ^a	Ref. Binding energy of Ag 3d _{5/2} (eV)
	Ag 3d _{5/2}	O 1s		
Ag/Al ₂ O ₃	368.0 368.5	531.2	0.76	Ag ₂ O 367.9 eV [34] Ag 368.4 eV [38]
Ag ₃ PO ₄ /Al ₂ O ₃	368.1	531.4	1.5	Ag ₃ PO ₄ 368.2 eV [35]
Ag ₂ SO ₄ /Al ₂ O ₃	368.2 367.8	531.3	1.1	Ag ₂ SO ₄ 368.3 eV [36] Ag ₂ O 367.9 eV [34]
AgCl/Al ₂ O ₃	368.3	531.4	0.5	AgCl 368.1 eV [37]

^a Atomic ratio corresponds to the ratio of apparent surface element content (at.%).

On the basis of the above characterizations, it is confirmed that the highly dispersed +1 oxide state silver species on the four silver catalysts are the active sites for the SCR of NO_x by ethanol. Furthermore, it is proposed that using silver precipitable compounds to prepare Ag catalysts may provide a method to fix and stabilize the silver species in the +1 oxide state.

4.3. In situ DRIFTS studies

4.3.1. The formation of enolic species on silver compound catalysts supported on Al₂O₃

The enolic species, originating from the partial oxidation of C₂H₅OH during the SCR, play an important role in the formation of the –NCO species as a key intermediate [24,25,39]. In our previous studies, we have proved that Ag participated in the formation of the adsorbed enolic species based on the results of DFT calculations of the vibrational frequencies and in situ DRIFTS spectra [25,39]. Therefore, we investigated the formation of enolic species on the various silver compound catalysts. Fig. 4(a)–(c) shows the in situ DRIFTS spectra of Ag₃PO₄/Al₂O₃, Ag₂SO₄/Al₂O₃ and AgCl/Al₂O₃, respectively, in a flow of C₂H₅OH + O₂ over the temperature range 473–773 K in the steady state. As shown in Fig. 4(a), peaks at 1633, 1579, 1466, 1416 and 1336 cm⁻¹ were observed on the surface of Ag₃PO₄/Al₂O₃, which are similar to those on the surface of Ag/Al₂O₃ found from our previous studies [24,25,39]. These peaks can be assigned to enolic species (1633, 1416 and 1336 cm⁻¹) [24,25,39] and acetate (1579 and 1466 cm⁻¹) [8,9,40]. Comparing the peak intensities of enolic species and acetate, we find that the enolic species was the main species in the temperature range of 523–773 K. For Ag₂SO₄/Al₂O₃ and AgCl/Al₂O₃ in Fig. 4(b) and (c), the adsorption peaks assigned to the enolic species (1633, 1416–1417 and 1327–1336 cm⁻¹) [24,25,39] and acetate (1576–1579 and 1464–1468 cm⁻¹) [8,9,40] were all visible in the temperature range of 473–773 K. It is reasonable that surface species on these catalysts show some similarity, because the Ag in all catalysts is in the +1 oxidation state, as discussed above. It is worth noting that the temperature range for which the enolic species was the main species was different for the three catalysts, that is, 523–773 K for Ag₃PO₄/Al₂O₃ and Ag₂SO₄/Al₂O₃, and 623–773 K for AgCl/Al₂O₃. Considering the different degrees of Ag dispersion on the various catalysts (Table 1), we conclude that highly dispersed Ag(I) is favorable for the formation of the enolic species.

4.3.2. Reaction mechanism of C₂H₅OH-SCR of NO_x over the silver compound catalysts supported on Al₂O₃

It was reported that the –NCO species was a vital intermediate for the SCR of NO_x over Ag/Al₂O₃, and its high reactivity resulted in a high efficiency of NO_x reduction by C₂H₅OH or hydrocarbons [6,8,19,40–43]. In our previous studies [24,25,39], it was found that the enolic species has a higher reactivity with NO + O₂ than acetate to form the surface –NCO species over Ag/Al₂O₃. In order to obtain the information on the reactivity of the surface enolic species over silver compounds supported on Al₂O₃, transient response experiments using in situ DRIFTS were performed. Fig. 5(a) shows the dynamic changes of in situ DRIFTS spectra of the adsorbed species on Ag₃PO₄/Al₂O₃ in a flow of NO + O₂ at 673 K. After exposing the catalyst to the flow of C₂H₅OH + O₂ for 60 min, very strong enolic species peaks were observed at 1633, 1416 and 1336 cm⁻¹, and acetate peaks were also observed at 1576 and 1464 cm⁻¹. Switching the feed gas to a flow of NO + O₂ resulted in the disappearance of the enolic species in 5 min. At the same time, new peaks appeared at 2231 and 2254 cm⁻¹, which are assigned to Ag–NCO and Al–NCO [6,8,19,40–43]. With the reaction time prolonged, the peaks at 1589 and 1300 cm⁻¹ for nitrate appeared [8,15,41,42]. It is noticed that the intensity of the –NCO species initially increased, reached a maximum, then decreased. The

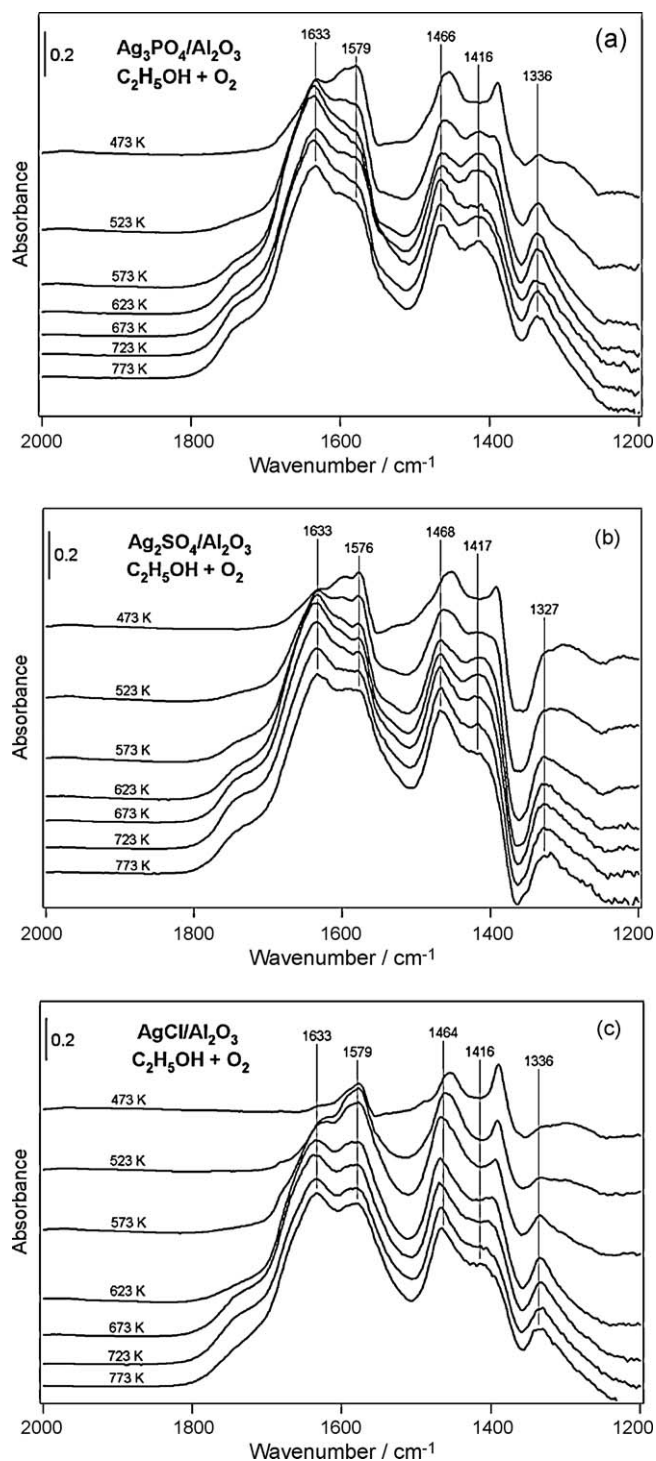


Fig. 4. In situ DRIFTS spectra of the silver compound catalysts supported on Al₂O₃ at various temperatures in a flow of C₂H₅OH + O₂. (a) Ag₃PO₄/Al₂O₃; (b) Ag₂SO₄/Al₂O₃; (c) AgCl/Al₂O₃. Conditions: C₂H₅OH, 1565 ppm; O₂, 10%; N₂ balance.

integrated areas of the peaks in Fig. 5(a) are displayed as a function of time in Fig. 5(b). Similar results were observed with the Ag₂SO₄/Al₂O₃ and AgCl/Al₂O₃ catalysts (results not shown). The connection between the formation of the –NCO species and the consumption of the enolic species strongly suggests the participation of the enolic species in the formation of the –NCO species, which further confirms our previous conclusion [24,25,39].

Based on the above results, the reaction mechanism of C₂H₅OH-SCR of NO_x was further investigated on the various silver

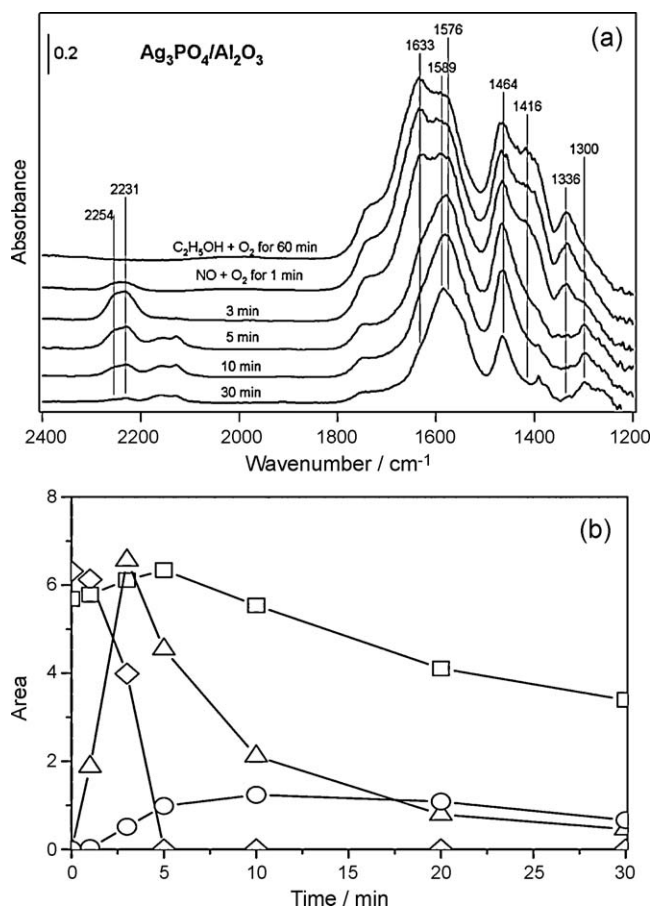


Fig. 5. (a) Dynamic changes of in situ DRIFTS spectra of the adsorbed enolic species on $\text{Ag}_3\text{PO}_4/\text{Al}_2\text{O}_3$ as a function of time in a flow of $\text{NO} + \text{O}_2$ at 673 K. Before the measurement, the catalyst was pre-exposed to a flow of $\text{C}_2\text{H}_5\text{OH} + \text{O}_2$ for 60 min at 673 K. Conditions: $\text{C}_2\text{H}_5\text{OH}$, 1565 ppm; NO , 800 ppm; O_2 , 10%; N_2 balance. (b) Time dependence of the integrated areas of the peaks for different adsorbed species in (a): (Δ) –NCO, 2197–2297 cm^{-1} ; (\diamond) enolic species, 1363–1437 cm^{-1} ; (\square) acetate, 1446–1500 cm^{-1} ; (\circ) nitrates, 1270–1313 cm^{-1} .

compound catalysts by in situ steady state DRIFTS. Fig. 6(a)–(c) shows the in situ DRIFTS spectra of three silver compound catalysts in a flow of $\text{NO} + \text{C}_2\text{H}_5\text{OH} + \text{O}_2$ over the temperature range of 473–873 K in the steady state. In the case of $\text{Ag}_3\text{PO}_4/\text{Al}_2\text{O}_3$ (Fig. 6(a)), several peaks appeared in the region of 1200–1800 cm^{-1} ; these peaks are attributed to the enolic species (1633, 1417 and 1336 cm^{-1}) [24,25,39], acetate (1576 and 1464 cm^{-1}) [8,9,40] and nitrate (1589 and 1300 cm^{-1}) [8,15,41,42]. In the range of 2400–2000 cm^{-1} , the –CN species (2158 cm^{-1}) was visible at 473–773 K; Ag–NCO (2231 cm^{-1}) was present at 523–773 K and Al–NCO (2254 cm^{-1}) was observed at 523–573 K [6,8,19,40–43]. Similar results were observed for $\text{Ag}_2\text{SO}_4/\text{Al}_2\text{O}_3$, as shown in Fig. 6(b). However, for the $\text{AgCl}/\text{Al}_2\text{O}_3$ catalyst in Fig. 6(c), no obvious –CN species (2158 cm^{-1}) appeared, while Al–NCO (2254 cm^{-1}) appeared at 573–673 K, and Ag–NCO (2231 cm^{-1}) was present at 723–773 K. It is supposed that the formation of bulk AgCl crystal lowered the dispersion of Ag and led to the low surface concentration of Ag–NCO, which was responsible for the somewhat lower apparent activity in the low temperature region 473–573 K as compared with the other three catalysts (Fig. 1). Based on the above results, we can conclude that the reaction mechanism of $\text{C}_2\text{H}_5\text{OH}$ -SCR of NOx over the Al_2O_3 -supported silver precipitable compound catalysts is very similar to that over the $\text{Ag}/\text{Al}_2\text{O}_3$ catalyst [14,15,24,25,39], and that the high dispersion of Ag(I) favored the reaction.

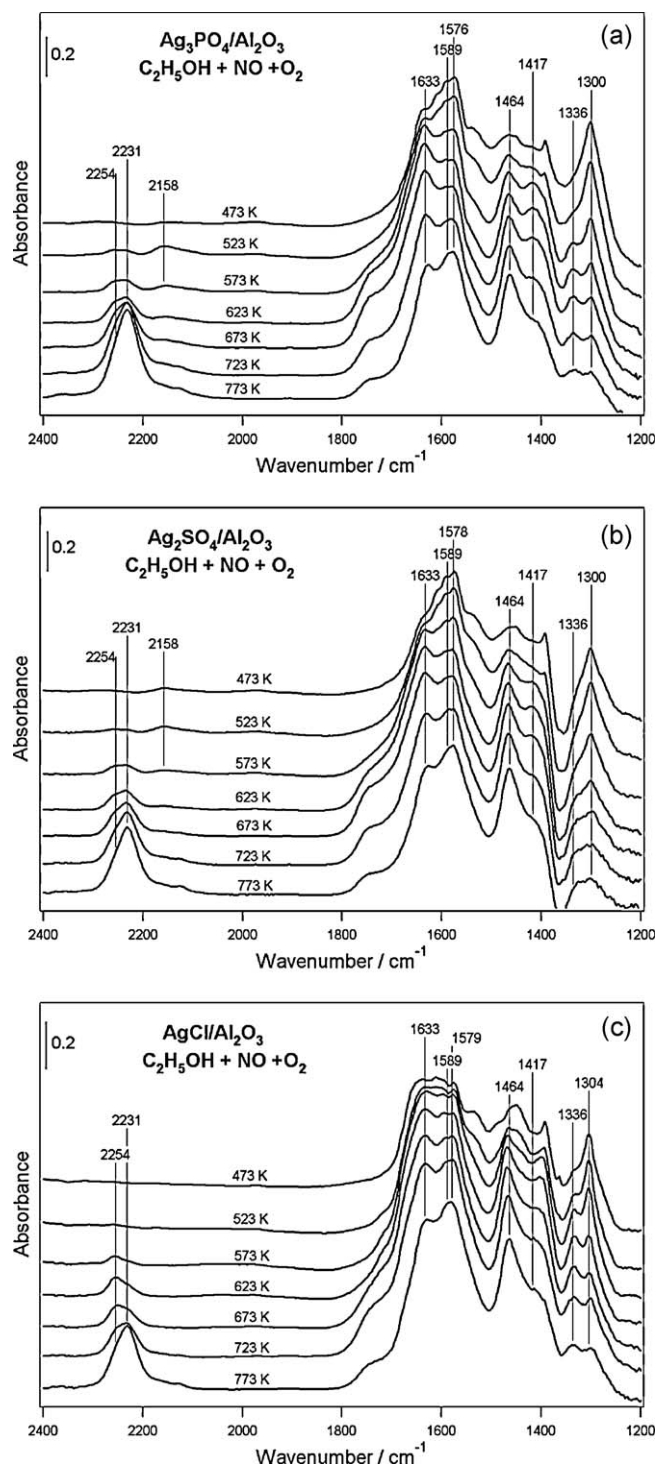


Fig. 6. In situ DRIFTS spectra of the silver compound catalysts supported on Al_2O_3 at various temperatures in a flow of $\text{NO} + \text{C}_2\text{H}_5\text{OH} + \text{O}_2$. (a) $\text{Ag}_3\text{PO}_4/\text{Al}_2\text{O}_3$; (b) $\text{Ag}_2\text{SO}_4/\text{Al}_2\text{O}_3$; (c) $\text{AgCl}/\text{Al}_2\text{O}_3$. Conditions: NO , 800 ppm; $\text{C}_2\text{H}_5\text{OH}$, 1565 ppm; O_2 , 10%; N_2 balance.

4.4. Washcoated honeycomb catalyst tests

On the basis of the above investigation, the $\text{Ag}_3\text{PO}_4/\text{Al}_2\text{O}_3$ and $\text{AgCl}/\text{Al}_2\text{O}_3$ washcoated honeycomb catalysts with stable properties were prepared, and activity tests for the SCR of NOx by ethanol were performed under the same conditions as for the powder catalysts, as shown in Fig. 7, respectively. The $\text{Ag}_3\text{PO}_4/\text{Al}_2\text{O}_3$ and $\text{AgCl}/\text{Al}_2\text{O}_3$ washcoated honeycomb catalysts were tested under

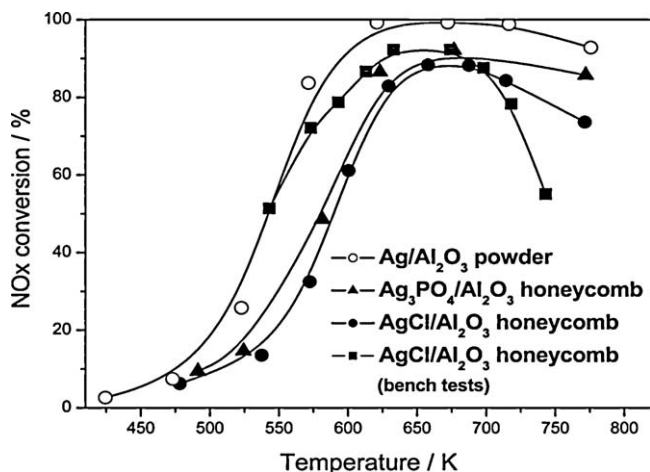


Fig. 7. NOx conversions for the SCR of NOx by C₂H₅OH over the (○) Ag/Al₂O₃ powder catalyst, (▲) Ag₃PO₄/Al₂O₃ washcoated honeycomb catalyst, (●) AgCl/Al₂O₃ washcoated honeycomb catalyst, and (■) AgCl/Al₂O₃ washcoated honeycomb catalyst bench tested on a diesel engine. Conditions: 800 ppm NO, 1565 ppm C₂H₅OH, 10% H₂O, 10% O₂, N₂ balance, GHSV = ~30,000 h⁻¹ or GHSV = ~30,000 h⁻¹ (bench tests).

50,000 h⁻¹ of GHSV and 0.008 g s cm⁻³ of W/F, while the powder Ag/Al₂O₃ catalyst was tested under 50,000 h⁻¹ of GHSV and 0.018 g s cm⁻³ of W/F. As expected, the NOx conversions over the washcoated honeycomb catalysts were similar to those with the Ag/Al₂O₃ powder catalyst (shown in Fig. 7). Of course, the maximum NOx conversion by the honeycomb catalysts decreased slightly compared to that of the powder catalysts, which is reasonable due to the shape difference and lower W/F values.

Since the precipitable silver compounds can be used as the active sites on Al₂O₃ for NOx reduction, this gives great opportunities for the preparation of monolith Ag/Al₂O₃ catalysts for practical use. Based on laboratory studies, a bench test was carried out using the monolith AgCl/Al₂O₃ washcoated honeycomb catalyst and C₂H₅OH as a reducing agent with a heavy duty diesel engine operating under practical conditions, as shown in Fig. 7, and a good performance was obtained. At the typical diesel engine exhaust temperature range, the conversion of NOx remained rather high at a GHSV of ~30,000 h⁻¹ (W/F = 0.013 g s cm⁻³). The highest NOx conversion reached 92.3% at an operating temperature of 673 K. The results are very close to the laboratory results, indicating the potential applicability for NOx reduction under real diesel engine exhaust conditions.

5. Conclusions

The activity of Ag(I) on various silver precipitable compound catalysts supported on Al₂O₃ (Ag₃PO₄/Al₂O₃, Ag₂SO₄/Al₂O₃ and AgCl/Al₂O₃) for the SCR of NOx has been confirmed using both powder and washcoated honeycomb catalysts. Sulfate, phosphate and chloride anions help to stabilize the Ag(I) species on the Al₂O₃ support and promote its intrinsic activity of NOx reduction, although the apparent activity could be affected by the dispersion of precipitated Ag(I) species. AgCl was observed to have a much higher TOF for NOx reduction than silver oxide, Ag₃PO₄ or Ag₂SO₄. The SCR reaction mechanism over the Al₂O₃-supported silver compound catalysts is very similar to that over the Ag/Al₂O₃ catalyst. Furthermore, the excellent performance of the monolith AgCl/Al₂O₃ washcoated honeycomb catalyst for the SCR of NOx using ethanol as the reductant has been confirmed in bench tests

using a heavy duty diesel engine. Therefore, we conclude that the silver precipitable compounds can be used to create and stabilize the active Ag(I) sites on Ag compound catalysts, and to facilitate the practical use of Ag/Al₂O₃ in the SCR of NOx by hydrocarbons.

Acknowledgements

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