Effect of Al_2O_3 phase on the catalytic performance for HCHO oxidation over Ag/Al_2O_3 catalysts

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Effect of Al₂O₃ phase on the catalytic performance for HCHO oxidation over Ag/Al₂O₃ catalysts

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Graphical Abstract



Highlights

- Ag species is selectively anchored on coordinated Al_{III} and Al_{V} sites in Ag/Al_2O_3 catalysts.
- The silver state and particle size strongly depends on the Al³⁺ chemical environment.
- OH groups adjacent to the coordinated Al_{VI} involve the formation of intermediates.
- Ag/ γ -Al₂O₃ exhibits higher activity for HCHO catalytic oxidation than Ag/ γ , θ -Al₂O₃.

Abstract

The effect of different crystalline phases of Al₂O₃ (γ -Al₂O₃, γ , θ -Al₂O₃) on HCHO oxidation over Ag catalysts is investigated, and the silver state and particle size strongly depend on the Al₂O₃ crystalline phase. The various coordinatively unsaturated Al³⁺ (Al_{III}, Al_V) involves in the formation of Ag-O-Al entities. Ag species is mainly anchored on Al_V sites for γ -Al₂O₃, whereas mainly on Al_{III} sites for γ , θ -Al₂O₃. The weaker interaction of Ag, O and Al_V on γ -Al₂O₃ compared with that of Ag, O and Al_{III} on γ , θ -Al₂O₃ and the larger surface area of γ -Al₂O₃ result in the formation of more Ag⁰ with high dispersion. The higher fraction of coordinated Al_{VI} on γ -Al₂O₃ provides more adjacent hydroxyl groups for HCHO adsorption and formation of intermediates. And the synergistic effect of OH group and the high activation ability for oxygen on smaller Ag⁰ particles give the high HCHO oxidation activity on Ag/ γ -Al₂O₃ (T₁₀₀=85°C).

Keywords: Ag/Al₂O₃, Crystalline phase, Coordinatively unsaturated Al, HCHO catalytic oxidation

1. Introduction

Exposure to indoor air containing formaldehyde to a certain extent may cause serious health hazards [1, 2]. Much effort has been devoted to eliminate HCHO, among which catalytic oxidation is one of the most effective methods [3-6]. Nobel metal-based catalysts, especially Pt and Au catalysts, exhibit high activities on formaldehyde oxidation at ambient temperature [7-10]. Recently supported Ag catalyst has been proved effective for HCHO catalytic oxidation by microstructure adjustment of metal particles and supports [9, 11-18]. However, it is still an inevitable challenge for practical application respect to the desires for lower temperature and economy. Therefore, to enhance the activity at low temperatures much study has focused on the microstructure and properties of the supports and active components.

Various supports have been employed on the HCHO catalytic oxidation, such as CeO₂, TiO₂, Co₃O₄, MnO₂, Fe₂O₃ etc., due to their oxygen storage capacity, acid-base properties, reactivity of surface hydroxyls or the strong interaction between supports and silver [3, 11, 13, 15, 18]. Transitional Al₂O₃, in recent years, is widely used as catalytic support in heterogeneous catalysis due to its surface acid-base properties and high surface area. It shows a significant effect on the stability of the active species involving in the catalytic process. Ag/Al₂O₃ catalyst exhibits the higher activity even than platinum group metals based catalysts for oxidant-free alcohol dehydrogenation [19]. The role Ag-O-Al entities over Ag-alumina catalysts for the SCR reaction reveals that the reaction rate is correlated with the amount of Ag-O-Al sites [20], and the effect

of the support on the formation and distribution of Ag species of Ag-based catalysts for NH_3 selective catalytic oxidation (NH_3 -SCO) has been documented [21] that the smaller Ag^0 particles (5 nm) with high dispersion obtained on Al_2O_3 support exhibit the highest performance for NH_3 conversion to N_2 .

It is found that alumina phases take a crucial role in the formation of active components of alumina-supported catalysts and then influence their performance [22, 23]. The surface structure of alumina usually changes with the phase determines the location of the active components. The terminal hydroxyl groups on the surface of γ -Al₂O₃ has been deduced to be responsible for Ag species anchoring [24]. Generally, for transitional alumina, the mixed crystalline phases are always observed since the preparation of Al₂O₃ is a process of phase transformation, for example, in which γ -Al₂O₃ and θ -Al₂O₃ may coexist in the structure of core and shell [25]. Alumina with different coordinatively unsaturated Al (three-, four-, five-coordinated) [26] possess various capacity for anchoring metal components into different coordinated Al sits, which will induce the variation of the metal nanostructure and properties [27]. However, there are few reports on the influence of different phases of Al₂O₃ on the activity of HCHO catalytic oxidation over Ag/Al₂O₃ up to now. Thus, it is essential to reveal their effects on the formation of Ag species and the performance of HCHO catalytic oxidation over Ag/Al₂O₃ catalysts.

In this work, we emphasize the necessity to understand different Al_2O_3 crystalline phases and their effects on the state and structure of Ag particles. The surface structure of Al_2O_3 supports and their influences on the performance for HCHO oxidation over Ag/Al_2O_3 catalysts are investigated.

2. Experimental Section

2.1 Catalyst preparation

Two kinds of Al₂O₃ supports (γ -Al₂O₃, γ , θ -Al₂O₃) were prepared by hydrothermal procedure according to the previous study [28, 29] and calcined at 500°C and 900°C for 2 h respectively. Ag/Al₂O₃ catalysts were prepared by impregnating Al₂O₃ with an aqueous solution of silver nitrate and dried at 80°C, followed by calcination at 500°C for 2 h. The obtained powder was squashed and crushed to get samples with mesh sizes of 20-40. The amounts of Ag loading were 8wt% nominally in as-prepared catalysts.

2.2 Characterization

Specific surface areas were obtained from the isotherms by employing the Brunauer–Emmett–Teller (BET) method in Quantachrome quadrasorb SI. The pore diameter distributions were calculated from desorption isotherms using the BJH (Barrett–Joyner–Halenda) model. Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku powder diffract meter using Cu K α ($\lambda = 0.1542$ nm) radiation and operating at 40 kV and 200 mA. The patterns were estimated by scanning 2 θ angles ranging from 20° to 80° for wide-angle XRD with a step size of 0.02°. Transmission electron microscopy (TEM) images were recorded using a Tecnai G2F30 S-Twin operating at 100 kV. UV–vis diffuse reflectance spectra were collected with SHIMADZU UV–2600 UV–vis spectrophotometer. X-ray photoelectron spectroscopy were measured on an ESCALAB250 X-ray photoelectron spectrometer (Thermo VG) using monochromatic X-ray source of Al K α (1486.6 eV) as excitation source under ultra-high vacuum. The binding energies were corrected by the carbon C (1s) binding energy at 284.6 eV.

HCHO-TPD (Temperature programmed desorption) and HCHO-TPSR (Temperature programmed surface reaction) tests were carried out on the in-situ

OmniStar 320 mass spectrometer. Prior to the adsorption of HCHO, the catalysts were pretreated by pure helium at 300°C for 30 min, and cooled to room temperature under helium. HCHO was introduced by helium for a certain time, and then the catalysts were purged with helium to remove the physisorbed HCHO molecules on the surface for 90 minutes. Subsequently, the temperature was raised up from RT to 450°C at 10°C min⁻¹ for HCHO-TPD in a continuous flow of helium, and from RT to 300°C at 10°C min⁻¹ for HCHO-TPSR in a continuous flow of helium and oxygen. The effluents from quartz reactor were detected on-line by mass spectrometer.

The catalytic oxidation of HCHO was tested in a fixed-bed flow reactor with 0.2 g of the catalyst under atmospheric pressure. By introducing nitrogen gas to a sealed bottle with trioxymethylene (99.5%, AcrosOrganics) in an incubator with an ice water mixture, gaseous HCHO was generated. The feed gas mixture consisting of 20 vol. % oxygen, ~ 200 ppm HCHO and balanced N₂ was introduced to the catalysts bed at a total flow rate of 30 mL/min. The apparent activation energy (E_a) was obtained from kinetic experiments, and the HCHO conversion was controlled within 16%. The conversion of HCHO to CO₂ was evaluated according to the formation of CO₂ as a function as follows:

$$X_{\rm HCHO}\% = \frac{[\rm CO_2]_{out}}{[\rm CO_2]_{total}} \times 100\%$$

The effluent gas CO_2 was analyzed by on-line gas chromatograph (GC 7890II, Tech comp, China) with FID detectors and a nickel catalyst converter.

²⁷Al MAS NMR experiments were performed on the Agilent DD2-500 MHz spectrometer at 130.2 MHz using a 4-mm MAS NMR probe with a spinning rate of 14 kHz. The spectra were accumulated for 120 scans with 2 s recycle delay. The chemical shifts were referenced to 1% Al (NO₃)₃ aqueous solution. The samples were not pretreated before NMR measurements in order to well elucidate the effect of

coordinatively unsaturated Al³⁺ on the anchoring of silver species.

In situ diffuse reflectance infrared Fourier transform spectroscopy (*in situ* DRIFTS) were recorded on a Thermos Nicolet iS 10 equipped with an MCT detector which is cooled by liquid nitrogen. Prior to the experiments, all the samples (ca. 10 mg in weight) were purged by N₂ for 30 min at 300°C, and then cooled to 30°C. The spectra of Ag/Al₂O₃ served as background were monitored in N₂ at different temperatures. The adsorption spectra of HCHO at 30°C were recorded in the HCHO/N₂ mixture for 30 min. Then the spectra for HCHO oxidation were collected in the flow of 20% O₂/N₂ at a rate of 30 ml/min at different temperatures.

3. Results and discussion

3.1 Structure and surface properties

The XRD patterns of different Al₂O₃ and Ag/Al₂O₃ samples are shown in Fig.1. One of the Al₂O₃ is typical of γ -Al₂O₃ phase (JCPDS Card No.10-0425), with peaks at 31.9°, 37.6°, 39.4°, 45.8°, 60.9°, 67.0°, denoted as γ -Al₂O₃. For the other sample, besides the peaks assigned to γ -Al₂O₃ phase, there are some peaks at 27.6°, 31.2°, 32.7°, 46.5°, 50.4°, 60.1° assigned to θ -Al₂O₃ phase [30]. Thus, this sample is a hybrid of θ -Al₂O₃ and γ -Al₂O₃, denoted as γ , θ -Al₂O₃. When the silver is loaded, the peaks at 20=38.2°, 44.3°, 64.5°, and 77.6° assigned to metallic silver emerge on the patterns of XRD, revealing the existence of metallic Ag in both Ag/Al₂O₃ samples. The diffraction peak intensity of Ag for Ag/ γ , θ -Al₂O₃ is much stronger than that for Ag/ γ -Al₂O₃, indicative of higher crystallinity of metallic Ag or larger Ag particle size on the former.

Solid–state nuclear magnetic resonance (NMR) technique as a sensitive probe for selected elements, that can detect the local structures despite of the crystallinity, has been employed to identify the local environment, e.g., coordinative numbers and bond

distance recent years [31-33]. The local coordination geometry information of the two kinds of Al₂O₃ supports was obtained to elucidate the distribution of Al atoms according to the empirical correlations between the ²⁷Al NMR parameters and structure features of aluminum compounds. The isotropic chemical shift, δ_{iso} of ²⁷Al nuclei is known to be strongly correlated to aluminum coordinated number. The fractions of Al_{IV}, Al_V and Alvi were evaluated by comparing of the peak areas of ²⁷Al MAS NMR spectra, and the results are shown in Fig.2. The chemical shifts at ca. 4, 11 ppm are assigned to Avi, ca.36 ppm is assigned to Al_V , and 60, 69 ppm are assigned to Al_W , respectively [31, 34]. The fractions of three kinds of coordinated Al on the two supports are listed in Table 1. Compared with γ , θ -Al₂O₃, γ -Al₂O₃ possesses higher proportions of Al_V (4.60% vs. 2.12%), Al_{VI}(68.0% vs.65.4%), and lower proportion of Al_{IV}(27.4% vs. 32.5%). When 8 wt% silver is loaded on Al₂O₃, the fraction of Al_V on Ag/ γ -Al₂O₃ catalyst decreases from 4.60% to 2.20%, while the fraction of Alvincreases from 68.0% to 70.6%. The certain amount of Ag is anchored on Alv to form Ag-O-Alvi entities [35]. No obvious change for Al_{IV} fraction is observed (27.4% to 27.2%). Differently, for Ag/ γ , θ -Al₂O₃, the spectrum shows fraction drops of $Al_V(2.12\% \text{ to } 1.18\%)$ and $Al_{VI}(65.4\% \text{ to } 61.9\%)$, but a significant fraction increase of $Al_{IV}(32.5\% \text{ to } 37.2\%)$.

It has been known that three-coordinated Al is not detectable by ²⁷AlNMR despite the fact that the three-coordinated Al on the surface is expected based on the bulk structure. F.R. Chen [31] have ascribed this to the high quadrupole coupling constants (QCCs) of the species, and concluded the conversion of Al_{III} into a higher coordination, such as tetra-coordinative Al when exposing to traces of oxygen or of water vapor. Similarly, Karl Sohlberg etc. [36] have proposed that when the structure is relaxed, it undergoes a reconstruction, in which the tri-coordinated Al atoms initially exist in the surface layer and then drop into the vacant octahedral interstices of the first subsurface

layer.

 Ag^+ can be anchored on the Al_{III} sites as the most reactive Ag species [37] for selective catalytic reduction of NO_x by ethanol. Deng, H. etc. proposed that Al_{III} sites are the precursors of the Ag-O-Al_{IV} entities [38]. Thus, in this work, the increase of A_{IV} proportion for Ag/ γ , θ -Al₂O₃ probably should be originated from the conversion of a certain amount Al_{III} into Al_{IV}, forming Ag-O-Al_{IV} entities after Ag addition. A little increment in proportion of Al_{IV} on γ -Al₂O₃ indicates the little Ag anchoring on Al_{III} sites for γ -Al₂O₃. Thus more coordinatively unsaturated Al_{III} exists on γ , θ -Al₂O₃ than on γ -Al₂O₃. To further understand this locating mechanism, Ag loading was decreased to 4 wt.% on γ -Al₂O₃ and the results of ²⁷Al NMR spectra (Table 1) show that Ag/ γ -Al₂O₃ possesses 27.8% Al_{IV}, little increase compared to γ -Al₂O₃ support; 2.7% Al_V, less than that of γ -Al₂O₃ support and 69.5% Al_V, higher than that of γ -Al₂O₃ support. It can be concluded that apart from a little fraction of Ag anchoring on Alm sites, Ag is primarily located on Alv sites, forming Ag-O-Alv, and give rise to the increment of Alv. Moreover, the fraction of Al_{IV} on 8wt.% Ag/ γ -Al₂O₃ (27.2%) is a bit lower than that on 4 wt.% Ag/ γ -Al₂O₃ (27.8%), indicative of the possibility that Ag-O-Al_{IV} bind Ag again to form (Ag-O)₂-Al_V. The formation of (Ag-O)₂-Al_V should result in the increase of the fraction of Alv. However, the fraction of Alv drops from 2.7% to 2.2%, suggesting more Ag is anchored on Al_V sites than on Al_{IV} sites. Therefore, the above data lead us to get the conclusion that Ag is mainly located on Al_V sites for γ -Al₂O₃, while on Al_{II} sites for γ , θ -Al₂O₃. Kwak, J. H. and An-Hui Lu etc. [39-41] have also concluded that the active component Pt is primarily anchored on coordinated Al_V sites of γ -Al₂O₃.

Summarily, the interactions between Ag, O and differently coordinated Al are the basic factor for determining the Ag anchoring sites, and the various fractions of coordinated Al³⁺ affect the distribution of Ag on coordinated Al³⁺. Based on above

results, Ag is preferentially anchored on Al_{III} and Al_V sites, and the Ag anchoring sites are mainly dependent on the fractions of Al_{III} and Al_V. Since γ -Al₂O₃ support possesses more proportion of Al_V and less proportion of Al_{III}, and then more Ag species are anchored on Al_V sites. While γ , θ -Al₂O₃ support has more proportion of Al_{III} and less proportion of Al_V, therefore, more Ag species are anchored on Al_{III} sites.

Fig. 3a shows the N₂ sorption isotherm of different Al₂O₃ supports. Both Al₂O₃ samples yielded type IV curves with H3-shaped hysteresis loops, indicative of the presence of closely packed slit pores. Compared to γ -Al₂O₃, γ , θ -Al₂O₃ has a sharp capillary condensation step at slightly higher relative pressures P/P₀=0.8-1.0, indicating the existence of larger sized pores than those of γ -Al₂O₃ and 9.7 nm for γ , θ -Al₂O₃, respectively (Fig. 3b). Table 2 displays the structure properties of the two Al₂O₃ supports and Ag/Al₂O₃ catalysts. It is found that γ -Al₂O₃ (158.1 m²/g). When Ag is loaded on alumina, the BET surface area becomes 308.0 m²/g for Ag/ γ -Al₂O₃ and 146.2 m²/g for Ag/ γ , θ -Al₂O₃. The slight increase of BET of Ag/ γ -Al₂O₃ after Ag addition is probably due to the formation of interparticle pores [42] or the presence of some Ag particles on the surface [13].

Transmission electron micrographs of the Ag/Al₂O₃ samples are shown in Fig.4. Both the alumina supports appear the similar lamellar morphology. 80 particles were selected for particle size statistical analysis. Compared with Ag/ γ -Al₂O₃, a handful of larger silver particles are observed on Ag/ γ , θ -Al₂O₃. Ag particles on Ag/ γ -Al₂O₃ are better controlled, displaying a narrower size distribution of 9-17 nm than those on Ag/ γ , θ -Al₂O₃ (11-23 nm). The mean particle size of Ag is around 13.0 nm for Ag/ γ -Al₂O₃ and 16.2 nm for Ag/ γ , θ -Al₂O₃ respectively (listed in Table 2). Moreover, it is found

that there are 55.6 percentage of Ag particles with size below 13 nm on Ag/ γ -Al₂O₃, which is much higher than that on Ag/ γ , θ -Al₂O₃ (only 28.4%). This result is in accordance with that of XRD patterns. Ag/ γ -Al₂O₃ possesses a higher dispersion (10.3%) of Ag particles than that of Ag/ γ , θ -Al₂O₃ (8.27%).

Previous study [43] has proved that the large external surface area benefits the dispersion of active components. The study from Park et al. [44] reveals that, among the various crystalline Al₂O₃ supported Pt catalysts, the highest and lowest Pt dispersion can be got from Pt/ γ -Al₂O₃ and Pt/ α -Al₂O₃ with the largest and smallest BET surface area, respectively. The crystalline degree of Al₂O₃ increases with the decrease of the BET surface area [45]. Additionally, it has been known that the interaction of Pt and Al_V contributes to small Pt particle size with high dispersion [39-41]. In comparison to γ , θ -Al₂O₃, the formation of more proportion of Al_V on γ -Al₂O₃ should be conductive to the higher dispersion of Ag on Ag/ γ -Al₂O₃. Therefore, the higher BET surface area of the lower crystalline support and the interaction between Ag and Al_V are responsible for well controlling Ag particles size and high dispersion of Ag on Ag/ γ -Al₂O₃.

XPS spectra of the two catalysts are displayed in Fig. 5. The deconvolution results of XPS spectra suggest the co-existence of Ag₂O and metallic Ag species. The Ag $3d_{5/2}$ binding energy (BE) at 368.7 eV for both Ag/ γ -Al₂O₃ and Ag/ γ , θ -Al₂O₃ is characteristic of metallic Ag [46], and BE at 367.7 eV or 367.8 eV belongs to Ag₂O [47]. The Al 2p XPS peaks are both symmetric, centered at 74.1eV with a FWHM of 2.20 eV and 74.0 eV with a FWHM of 2.06 eV for catalysts Ag/ γ -Al₂O₃ and Ag/ γ , θ -Al₂O₃ respectively. The binding energy shifts 0.2 and 0.3 eV to lower BE compared with the standard binding energy (74.3 eV), indicative of the change of electronic valence of Al-O bond due to the interaction between Al, O and Ag [48], and the electric density is transferred from Ag to Al. Correspondingly, Ag shows an increase in ionic

character. The stronger the interaction of Al, O and Ag, the lower BE the Al-O bond shifts to. Thus, it can be concluded that the interaction of Al, O and Ag on Ag/ γ , θ -Al₂O₃ is stronger than that on Ag/ γ -Al₂O₃. Additionally, the width of the half peak (FWHM) of the both catalysts become larger than that of the standards (1.41 eV), which might be due to the incorporation of Ag particles into the alumina lattice [42] or Ag clusters screening on the alumina surface within a depth of about 20 Å [49]. These results also provide the valid evidences for the strong interaction between Ag and Al₂O₃ supports. In the deconvoluted O 1s XPS spectra, the peak at 531.2 eV with FWHM of 1.6 eV, is attributed to the lattice oxygen of Al₂O₃, and the peaks at 532.4 and 532.5 eV belong to the oxygen of surface hydroxyl (O_{OH}) groups [50]. Ag/ γ -Al₂O₃ shows a higher molar ratio of O_{OH}/O_{total} (77.9%) than that of Ag/ γ , θ -Al₂O₃ (73.5%).

UV-vis spectra shown in Fig. 6 reveal the valence state of Ag supported on Al₂O₃. For the both samples, the obvious peaks at 220 nm is ascribed to Ag⁺ [20, 21, 51] and the bands ranging from ca. 270 to 335 nm are ascribed to Ag_n^{δ +} [20, 21]. The bands at 350 nm and 450 nm are due to Ag⁰ clusters [43, 49]. Thus, it can be concluded that both Ag oxide and metallic Ag exist on Ag/Al₂O₃ combining XPS and UV-vis results. The broad and asymmetric peak of Ag/ γ -Al₂O₃ between 350 and 450 nm is owing to the multiformity of Ag⁰ particles [21]. It can be found from the deconvolution results that the percentage of Ag⁰ in total Ag species is 83.8% and 33.6% for Ag/ γ -Al₂O₃ and Ag/ γ , θ -Al₂O₃, respectively. Ag/ γ -Al₂O₃ possesses higher proportion of metallic silver than Ag/ γ , θ -Al₂O₃; whereas the latter has higher proportion of Ag oxide.

It has been observed from ²⁷Al NMR that silver species are anchored on different coordinated Al^{3+} sites for different Al_2O_3 , which will result in the different structure and electron properties of silver species due to the different interaction between metal and Al_2O_3 supports [52]. Ag/ γ -Al₂O₃ possesses more fractions of Ag-O-Al_{Vk} while Ag/ γ , θ -

Al₂O₃ possesses more Ag-O-Al_{IV} entities after Ag addition. It has been known that five-, four- and three-coordinate Al³⁺ ions are assigned to Lewis sites in an order of increasing acid strength [53]. When Ag is stabilized on coordinatively unsaturated Al via O, the electrons density would flow from Ag toward O and Al, therefore, the transferring electron density should be greater on stronger acid sites than on weaker ones. This means the transferring electron density is higher on Al_{III} than that on Al_{IV} or Al_V. The study of Hua Deng [38] on the DFT of structure of Ag/ γ -Al₂O₃ revealed that in comparison with Ag-O-Al_{IV}, Ag-O-Al_{VI} has the weaker Ag-O bonds, which meant metallic Ag is liable to present on the Al_V sites, and Ag⁺ tends to form on the Al_{III} sites. Therefore, Al electronic environment affects the Ag valence state due to the different interaction intensity between Ag and various coordinative Al³⁺ (described in scheme 1). For the two supports, the weaker interaction between Ag, O and Al_V of γ -Al₂O₃ benefits the formation of more metallic Ag (Fig.5 and Fig.6), while the stronger interaction between Ag, O and Al_{III} of γ , θ -Al₂O₃ results in more Ag⁺ formation (Fig.5 and Fig.6) during the process of calcination of the catalysts.

3.2 HCHO adsorption and catalytic activity over Ag/Al₂O₃ catalysts

HCHO-TPD profiles (m/z=30) of both catalysts derived from different Al₂O₃ supports are shown in Fig. 7. Ag/ γ -Al₂O₃ shows higher HCHO adsorption capacity than Ag/ γ , θ -Al₂O₃, which should be related with the stronger interaction between HCHO and the catalyst as well as the surface structures of Al₂O₃. The larger BET surface area benefits exposing the more adsorption sites, and the appropriate pore volume are critical to allow guest reactant molecules to diffuse into the host Al₂O₃ [29]. Little CO₂ is generated during the process of HCHO-TPD experiments (not shown here). Obviously, the whole process of HCHO adsorption depends on the physical and chemical

properties of the surface of Al₂O₃ supports.

During the HCHO-TPSR experiments, no CO₂ generation on Al₂O₃ supports is observed. HCHO-TPSR over Ag/Al₂O₃ catalysts profiles are shown in Fig. 8. When O₂ is introduced, a large amount of CO₂ is observed on Ag/Al₂O₃ catalysts. In consideration of little CO₂ generation during the process of HCHO-TPD, it is deduced that the gas oxygen species plays an essential role in HCHO oxidation and the activation of gas oxygen species should be related with silver species. It is noticed that the amount of CO₂ generation on Ag/ γ -Al₂O₃ is much larger than that on Ag/ γ , θ -Al₂O₃, which should be owing to the larger amount of adsorbed HCHO and easy activation of oxygen species by more small-sized metallic Ag species on the former.

The catalytic performance of Ag/Al₂O₃ catalysts for HCHO oxidation on fixed bed is shown in Fig. 9, and it is found that the conversion of HCHO to CO₂ increases with the temperature. Ag/ γ -Al₂O₃ catalyst exhibits the higher catalytic activity than Ag/ γ , θ-Al₂O₃ and reaches 100% of conversion at 85°C (Fig. 9(a)). The long-term tests of Ag/ γ -Al₂O₃ and Ag/ γ -Al₂O₃ catalysts for HCHO oxidation were carried out at 75°C and 85°C respectively, and the results are shown in Fig. 9 (b). Both the Ag/Al₂O₃ catalysts exhibit the excellent reaction stability. Ag/ γ -Al₂O₃ remains 36% conversion of HCHO and Ag/ γ , θ -Al₂O₃ remains 25% conversion of HCHO for 24 h. Fig. 9 (c) shows the Arrhenius plots of HCHO oxidation over Ag/Al₂O₃ samples. The activation energies (*E_a*) are obtained based on the slopes of the curves between ln(R) versus 1000/T. The activation energy of Ag/ γ -Al₂O₃ is 56.0 KJ/mol, much lower than that of Ag/ γ , θ -Al₂O₃ (100.5 KJ/mol). The activities of both catalysts dramatically decrease when the reaction is undertaken with water vapor (50% RH), which is probably owing to the adsorption competition between water and HCHO. The activity of Ag/ γ -Al₂O₃ is still higher than that of Ag/ γ , θ -Al₂O₃ at lower temperatures (<120°C).

It is reported that the addition of metallic Ag contributes to the activation of oxygen species and then improves HCHO catalytic oxidation activity at low temperature [3], and the formation of small and highly dispersed Ag particles will enhance the catalytic activity for HCHO oxidation [17]. Therefore, the large amount of relatively smaller metallic Ag particles with narrow size distribution on Ag/γ -Al₂O₃ should be responsible for its higher activity.

3.3 in situ DRIFTS study of HCHO catalytic oxidation

The adsorption spectra of complexes formed on various Ag/Al_2O_3 catalysts were recorded by in situ DRIFT spectrometer. After exposed to HCHO and N₂ mixture gas for 30 minutes at 30°C, the similar bands appear on the both Ag/ Al₂O₃ catalysts at 3019, 2945, 2867, 2848, 2795, 2743, 2234, 2200, 2130, 1690, 1551/1585, 1492, 1403, 1308, 1229, 1167, 1067, 963 cm⁻¹ (Fig. 10). The negative features at 3648-3788 cm⁻¹ for Ag/ γ -Al₂O₃ and 3648-3775 cm⁻¹ for Ag/ γ , θ -Al₂O₃ should be due to the consumption of the OH groups [53, 54] on the surface arising from the interaction of adsorbed HCHO with the catalysts surface. These OH groups are corresponded to the different terminal or bridging species bound to aluminum cations in different coordination [53, 54]. The intensity of the negative peaks for Ag/γ - Al_2O_3 catalyst is stronger than that of Ag/γ , θ -Al₂O₃ catalyst, indicating that a larger amount of OH group is consumed on the former for the formation of the intermediates. The strongest negative band is observed at ca. 3730-3745 cm⁻¹. E. V. Kul'ko [54] declared that the bands of 3730-3735cm⁻¹ are corresponded to the bridging OH groups on octahedral Al ions. Liu etc. [53] concluded that pyridine adsorbed on the weak Lewis acid sites is interacting with neighbor OH groups at 3729 cm⁻¹, which belong to bridging OH groups on Alv, Lundie etc. [55] ascribed 3730 cm⁻¹ to a hydroxyl bridging Al_{IV} and Al_{VI}. Although the assignment of the bands at 3730-3745 cm⁻¹ remains controversial, the accordant result shows its

correlation with OH groups on Al_{VI}sites. Therefore, it is deduced that formaldehyde molecules are adsorbed on the Lewis acid sites via the oxygen on HCHO [56], and the H of HCHO or the intermediates interacts with adjacent hydroxyl groups mostly on the coordinated Al_{VI}sites. Ag/ γ -Al₂O₃ catalyst possesses higher fraction of coordinated Al_{VI}, and should provide more adjacent hydroxyl groups during HCHO adsorption process than Ag/ γ , θ -Al₂O₃.

Additionally, several bands belonging to the adsorbed HCHO are detected at 2848, 2795, 1167 cm⁻¹. Meanwhile the peaks at 2743 cm⁻¹ ascribed to combination of δ (CH) and v_a (OCO) in formate [8, 56-58], and two bands at ca.1551, 1585 cm⁻¹ on the two catalysts respectively due to v(OCO) of formate species [16, 59, 60] are observed. Dioxymethylene (DOM) species (2945, 2867, 1492, 1403, 1308, 1067 cm⁻¹) [56, 61] and methoxy group (3019 cm⁻¹) form during HCHO adsorption process. It is worthy noted that the weak bands at ca. 1474, 963 cm⁻¹ are assigned to polyoxymethylene (POM) [56], arising from the polymerization of DOM [51]. The bands at 1690 and 1229 cm⁻¹ correspond to the C=O stretch and OH bend of HCOOH respectively [58]. Meanwhile adsorbed CO (2234, 2200, 2130 cm⁻¹) appears on the both catalysts. The bands at 2234, 2200 cm⁻¹ can be ascribed to CO interacting with Lewis acid sites that belong to corner of tri-coordinated and tetra-coordinated Al [54, 62, 63], and the band at 2130 cm⁻¹ belongs to physisorbed CO molecules or H-bonded (CO)_H, respectively [63, 64].

After the adsorption of HCHO for 30 min, $20\%O_2/N_2$ is introduced at different temperatures and the spectra are recorded. For Ag/ γ -Al₂O₃ catalyst (Fig.11 (a)), the intensities of all the peaks gradually decrease as O₂ is introduced at 30°C. When the temperature rises up to 90°C, methoxy (3019 cm⁻¹) and formate (2743 cm⁻¹) species almost disappear. All the peaks disappear with further increasing the temperature to

110°C. That gives an evidence of complete transformation of the intermediates which originate from HCHO adsorption. In addition, a perturbation at ca.1642 cm⁻¹ attributed to adsorbed water is observed. This should result from the intermediates conversion to CO_2 and H_2O on the surface of the catalyst during the oxidation process. Moreover, it can be concluded that POM, DOM, and adsorbed HCHO species are difficult to be oxidized than methoxy groups and fomate species.

For Ag/ γ , θ -Al₂O₃ (Fig.11 (b)), when 20%O₂/N₂ is introduced, the intensities of methoxy (3019 cm⁻¹), DOM (2945, 2867, 1492, 1403, 1308, 1067 cm⁻¹), formate (2743 cm⁻¹), adsorbed formaldehyde (2795, 1167 cm⁻¹) and formic acid (1229 cm⁻¹) decrease with the increase of the reaction temperature. Meanwhile the band at 2965 cm⁻¹ assigned to δ (CH) + ν_{as} (OCO) in HCOO_(a) of bidentate formate [59, 60] emerges at 50°C, and the intensity reaches to maximum at 80°C, then decreases at higher temperature, remaining even at 150°C. The characteristic bands of POM (2980, 1118, 1096 cm⁻¹) and H₃CO₂ (2952, 1192 cm⁻¹) show the same trend. The intensities of these bands belonging to bidentate formate, POM and H₃CO₂ increase at the cost of the decrease of those of DOM (2867, 1408, 1308, 1067 cm⁻¹). Thus, it can be inferred that bidentate formate and H₃CO₂ originate from the DOM and methoxy oxidation respectively. That means the formation of formate and methoxy is due to a Cannizzaro-type disproportionation of DOM. These results also prove that DOM species are not completely oxidized on Ag/ γ , θ -Al₂O₃ when O₂ is introduced and temperature rises up (below 150°C) due to its weak activation ability of oxygen.

Based on the above results and conclusions of previous studies [56, 65], the possible process of formaldehyde catalytic oxidation on Ag/Al_2O_3 is speculated as follow:

 $HCHO + O_s \longrightarrow H_2CO_2$

 $H_{2}CO_{2} + OH_{s} \longrightarrow HCOO + H_{2}O$ $H_{2}CO_{2} \longrightarrow HCOO + CH_{3}O$ $H_{2}CO_{2} + O_{s} \longrightarrow H_{2}O + CO_{2}$ $HCOO + O_{s} \longrightarrow CO + H_{2}O$ $CH_{3}O + O_{s} \longrightarrow CO + H_{2}O$ $CO + O_{s} \longrightarrow CO_{2}$

During the HCHO adsorption and oxidation process, the adsorbed HCHO forms DOM; DOM is converted to formate by consuming OH groups, or decomposes to formate and methoxy species via disproportionate reaction; DOM is oxidized to CO₂; and formate and methoxy are oxidized to CO and water, finally CO is oxidized to CO₂.

The higher ability of the electron-donation of metallic Ag than that of Ag⁺ results in the higher ability of activation and dissociation of molecular oxygen for Ag/ γ -Al₂O₃, [66]. Besides, smaller size Ag particles expose more active sites than the larger ones, which may facilitate the adsorption and activation of oxygen [43], therefore, Ag/ γ -Al₂O₃ with more fraction of small size metallic Ag particles exhibit better catalytic capacity for HCHO oxidation than Ag/ γ , θ -Al₂O₃.

To sum up, the coordinatively unsaturated Al on different crystalline phase play pivotal roles in the state and size of the active components (Scheme 1). The various coordinatively unsaturated Al^{3+} species (Al_{III} and Al_{V}) acts as electron acceptors in the process of Ag addition, and determines the interactions between Al, O and Ag. These interactions are conducive to forming and stabilizing the Ag species. Since Al_{III} is more liable to picking up the transferring electrons than Al_{V} , the interaction between Al_{III} , O and Ag is stronger than that between Al_{V} , O and Ag. The former benefits the formation of Ag⁺, while the latter contributes to the formation of Ag⁰ during the process of impregnation and calcination. Compared to Ag/γ , θ -Al₂O₃, Ag/γ -Al₂O₃ possesses higher content of Al_v, and thus possess more metallic Ag. Moreover, the higher BET of Ag/ γ -Al₂O₃ also contribute to Ag dispersion, formation of smaller size Ag particles and HCHO adsorption. By consuming more OH group, larger amounts of intermediates form on Ag/ γ -Al₂O₃ than on Ag/ γ , θ -Al₂O₃, which results in the higher activity of HCHO oxidation combining with the higher ability of adsorption and activation of oxygen on more content of smaller metallic Ag particles with fine dispersion.

4. Conclusions

In this work, the physicochemical properties of different phase of alumina supports and Ag/Al₂O₃ samples were remarked, and their catalytic performance for HCHO oxidation is investigated. Ag/ γ -Al₂O₃ catalyst shows the higher performance for formaldehyde oxidation (T₁₀₀ = 85°C) than Ag/ γ , θ -Al₂O₃ (T₁₀₀ = 130°C).

The Al chemical environment of different phase Al₂O₃ determines Ag state and particles size, and thus the different catalytic activity for HCHO oxidation. Ag species is mainly anchored on Al_V sites for γ -Al₂O₃, forming Ag-O-Al_{VI} entities; while on Al_{III} sites for γ , θ -Al₂O₃, forming Ag-O-Al_{IV} entities. The stronger interaction for Ag-O-Al_{IV} entities leads to the formation of more Ag⁺ species, and more Ag⁰ with high dispersion is observed on γ -Al₂O₃. Additionally, higher fraction of coordinated Al_{VI} on γ -Al₂O₃ provides more adjacent hydroxyl groups for HCHO adsorption and formation of intermediates. The high HCHO oxidation activity on Ag/ γ -Al₂O₃ should be related with the synergistic effect of OH group and the high activation ability of oxygen species on of smaller Ag⁰ particles with high dispersion.

Here we highlight the nature of coordinatively unsaturated Al_{III} and Al_V of Al_2O_3 and the interaction between Ag and Al_2O_3 with different crystalline phase. The further investigation and profound understanding are essential for catalyst design in specific

applications.

CRediT author statement

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Validation, Conceptualization, Writing-Reviewing and Editing

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Samples	Al _{IV} (%)	Al _V (%)	Alvi(%)
γ- Al ₂ O ₃	27.4	4.60	68.0
4% Ag/ γ -Al ₂ O ₃	27.8	2.70	69.5
8%Ag/γ- Al ₂ O ₃	27.2	2.20	70.6
γ , θ - Al ₂ O ₃	32.5	2.12	65.4
8%Ag/γ,θ-Al ₂ O ₃	37.2	1.18	61.9

Table 1 Al coordinated distribution of different Al ₂ O ₃ and Ag/Al ₂ O ₃ sample	Table	1 Al	coordinated	distribution	of different	Al ₂ O ₃ ar	nd Ag/Al ₂ C	O ₃ sample
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Samples	BET surface area (m²/g)	Pore volume (m ³ /g)	Average pore diameter (nm)	Ag mean particle size(nm) ^a	Ag dispersion (%) ^b
γ-Al ₂ O ₃	262.0	0.537	5.657		
Ag/γ - Al_2O_3	308.0	0.518	4.347	13.0	10.3
γ,θ-Al ₂ O ₃	158.1	0.569	9.663		
$Ag/\gamma, \theta$ - Al_2O_3	146.2	0.634	9.572	16.2	8.27

Fable 2 The stru	cture properties o	f different Al ₂ O ₃ and Ag/	Al ₂ O ₃ samples
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^a Determined by HRTEM. ^b Ag crystallites are assumed to be spherical, the relationship between diameter(d) and dispersion D, is d (nm) =1.34/D [67].

Figures Caption

Fig. 1. XRD patterns of different Ag/Al₂O₃ catalysts.

Fig. 2. ²⁷Al NMR of Al₂O₃ and Ag/Al₂O₃ catalysts.

Fig. 3. N₂ adsorption-desorption curves for different γ -Al₂O₃ materials (a) and pore size distribution (b).

Fig. 4. TEM images of (a) Ag/γ - Al_2O_3 , (b) Ag/γ , θ - Al_2O_3 and corresponding particles size distributions of (c) Ag/γ - Al_2O_3 , (d) Ag/γ , θ - Al_2O_3 .

Fig. 5. XPS spectra of different Ag/Al₂O₃ catalysts.

Fig. 6. UV-vis spectra of different Ag/Al₂O₃ catalysts.

Fig. 7. HCHO-TPD profiles (m/z=30) of different Ag/Al₂O₃ catalysts.

Fig. 8. Profiles of CO₂ generation (m/z=44) during HCHO-TPD and HCHO-TPSR experiments over different Ag/Al₂O₃ catalysts.

Fig. 9. (a) Activity, (b) stability and (c) Arrhenius plots of the intrinsic reaction rate constants of HCHO conversion over different Ag/Al_2O_3 catalysts.

Fig. 10. DRIFT spectra of catalysts after exposed to a flow of HCHO+ N_2 for 30 min at room temperature.

Fig. 11. In situ DRIFT spectra of different Ag/γ -Al₂O₃ catalyst in a flow of gas mixture of O₂ and N₂ (a) Ag/γ -Al₂O₃, (b) Ag/γ , θ -Al₂O₃.

Scheme 1 Possible Ag anchoring mechanism of Ag/Al₂O₃.





Fig. 2



Fig. 3



Fig. 4



Fig. 5



























Scheme 1

