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The performance of Ag doped V_2O_5 - TiO_2 catalyst on the catalytic oxidation of gaseous elemental mercury

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To improve the catalytic oxidation ability for gaseous elemental mercury (Hg^0), silver was introduced to V_2O_5 - TiO_2 catalysts. The catalysts were prepared by an impregnation method with various additives to obtain well distributed silver nanoparticles on the carrier. It was found that doping silver onto V_2O_5 - TiO_2 can significantly improve the catalytic oxidation efficiency of Hg^0 , and the redox temperature range for Hg^0 oxidation was enlarged markedly (150–450 °C). The addition of polyvinylpyrrolidone (PVP) during the preparation of the catalysts can improve the dispersion of silver nanoparticles more effectively, which resulted in a higher Hg^0 oxidation efficiency up to 90%. However, the oxidation of Hg^0 on the catalyst was slightly inhibited due to the larger silver nanoparticles when the ionic liquid (IL) [bmim][BF₄] was used as the additive. The characterization results indicated that V can be induced to a higher oxidation state in the presence of silver nanoparticles, and the transformation trend of TiO_2 from the anatase to rutile phase caused by Ag can be minimized in the presence of PVP or ILs. Meanwhile, the mechanisms of the elemental mercury oxidation at various temperature ranges were discussed.

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1. Introduction

Mercury emitted from coal-fired power plants has raised much concern in recent years because of its volatility, persistence and bioaccumulation.^{1,2} In order to protect human health and the environment from emissions of mercury, the Minamata Convention on Mercury was adopted in October 2013.³ In addition, the U.S. EPA promulgated a federal Mercury and Air Toxics Standard (MATS) to limit mercury emissions from power plants in December 2011.⁴ China is regarded as one of the largest countries of the anthropogenic mercury emissions.⁵ Therefore, it is imperative to make great efforts to reduce mercury emissions from coal-fired power plants.

The mercury in coal-fired flue gas is a mixture in its speciation, which can be classified into three forms: elemental mercury (Hg^0), oxidized mercury (Hg^{2+}) and particulate-bound mercury (Hg^p),⁶ which are mainly dependent on the combustion conditions and the chlorine content in the coal. Oxidized mercury (Hg^{2+}) and particulate-bound mercury (Hg^p) can be removed by existing air pollution control devices, such as an electrostatic precipitator (ESP) or a wet flue gas desulfurization (WFGD) system.^{7,8} In contrast, elemental mercury

(Hg^0) is difficult to remove from flue gas due to its high equilibrium volatility and low solubility in water.⁹ Therefore, it is important to develop effective technologies to remove Hg^0 . In recent years, lots of research on the capture or oxidization of Hg^0 has been performed,⁸ and the catalytic conversion of Hg^0 to its oxidized form by some catalysts is considered to be an effective method for Hg^0 control.

V_2O_5 - TiO_2 has been widely used as a catalyst for various purposes due to its low activation energy and strong transition metal-support interaction, and its use has also been attempted for the catalytic oxidation of elemental mercury.^{10,11} However, Hg^0 oxidation over V_2O_5 - TiO_2 catalysts appeared to be less effective at low temperatures or with low HCl concentration in the flue gas.¹² Therefore, how to enhance the catalytic activity for Hg^0 oxidation has become one of the key points for mercury emission control. Silver has long been recognized as an effective catalytic component.^{13,14} Adding silver to the V_2O_5 - TiO_2 catalyst might promote the reaction because Ag could generate electrophilic oxygens to facilitate the redox process.¹⁵ Zhang *et al.* showed that the addition of silver to V_2O_5 greatly decreased the surface acidity and increased the redox ability of the catalyst, leading to increased conversion of toluene.¹⁶ Meanwhile, Ag has even been employed as the sorbent to capture Hg^0 by means of amalgam at low temperature in previous studies,^{17,18} but research with Ag as the active catalyst for Hg^0 oxidation in the presence of HCl at various temperatures has never been reported.

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In addition, silver atoms are often ready to coalesce into oligomers, which will cause the formation of larger clusters or even precipitates during the process of preparation and calcination.¹⁹ However, the catalytic properties of Ag nanoparticles are directly related to their size and dispersion, and uniformly dispersed Ag nanoparticles with small size are ideal for high catalytic performance due to their large surface area.^{20,21} Therefore, how to prepare highly dispersed Ag nanoparticles loaded onto a support is one of the key points to solve.

It has been reported that using any proper additive can inhibit the agglomeration of silver particles, and ionic liquids (ILs) and polyvinylpyrrolidone (PVP) are common reagents for such a purpose.^{22,23} PVP can be employed as a stabilizer because it can prevent Ag nanoparticles from agglomerating through the steric effect. Besides, the electron lone pairs on imide groups in PVP can easily promote the nucleation of metal ions,²⁴ so adding PVP can be treated as a physico-chemical method. ILs can stabilize metal nanoparticles by forming a protective layer surrounding the nanoparticles, and can be regarded as physical stabilizers.²⁵ Escobar *et al.* synthesized Pt colloidal nanoparticles by simultaneous chemical reduction of metallic salts in the presence of PVP as a protecting agent, and the Pt colloidal nanoparticles were uniform and highly ordered when deposited onto multi-walled carbon nanotubes.²⁶ In addition, Wang *et al.* found that silver nanoparticles (AgNPs) can be well decorated onto graphene nano-sheets by adding an ionic liquid.²⁵

Briefly, silver has been tentatively employed to improve the catalytic performance of V-Ti catalysts for the oxidation of Hg⁰. Meanwhile, in order to obtain well dispersed silver nanoparticles doped onto the V₂O₅-TiO₂ catalysts, the ionic liquid [bmim][BF₄] and PVP were employed as additives for the preparation of the catalysts. The physical and chemical properties and Hg⁰ oxidation efficiency of various catalysts at low HCl concentration were studied. In addition, the involved catalysis mechanisms were discussed.

2. Experimental section

2.1 Materials

Commercially available TiO₂ powder (Degussa P25) was mainly used as the carrier of various catalysts, which was a standard material for all purposes and contained anatase and rutile phases in a ratio of about 3 : 1. All chemicals used for catalyst preparation were of analytical grade, and purchased from Sigma-Aldrich Co. and Sinopharm Chemical Reagent Co. The gases of SO₂ (10 000 ppm), and HCl (2000 ppm) were provided by Dalian Date Gas Co.

2.2 Preparation of catalysts

Catalysts were prepared by an impregnation method, and included V₂O₅-TiO₂, Ag-TiO₂, Ag-V₂O₅-TiO₂, Ag-V₂O₅-TiO₂-[bmim][BF₄] and Ag-V₂O₅-TiO₂-PVP. An appropriate amount of P25 was added to ammonium vanadate solution and stirred for 1 h. This was marked as solution A. The [bmim][BF₄]

or PVP was dissolved in water, then AgNO₃ precursor was added, and the mixed solution was stirred for 6 h at room temperature. This was marked as solution B. Solution B was added dropwise into solution A and the mixture was stirred constantly for 2 h. Then the mixed solution was evaporated and dried using rotary evaporation apparatus, and finally calcined in a muffle furnace (5 h, 500 °C). The V₂O₅-TiO₂, Ag-TiO₂, Ag-V₂O₅-TiO₂, Ag-V₂O₅-TiO₂-[bmim][BF₄] and Ag-V₂O₅-TiO₂-PVP catalysts are labeled V-Ti, Ag-Ti, Ag-V-Ti, Ag-V-Ti(IL) and Ag-V-Ti(PVP). The proportion of the V and Ag to TiO₂ is on the basis of the atom percentages, such as V(x%)-Ti represents V₂O₅/TiO₂ mole ratio, and the proportion of 1% was omitted.

2.3 Catalytic activity evaluation

The catalytic activity was evaluated in a simulated gas preparation system and catalytic reaction device, in which a cold vapor atomic absorption spectrometer (CVAAS) and an online data acquisition system were employed. The simulated gas system and catalytic reaction device included eight mass flow controllers to prepare simulated flue gas compositions and a fixed-bed reactor (a quartz tube with an inner diameter of 6 mm, and a tube type resistance furnace). The catalyst (40–60 particle meshes) was inserted into the quartz tube and fixed with quartz wool. Hg⁰ vapor was prepared from the Hg⁰ permeation unit and was blended with the gases before they entered the reactor. The concentration of elemental mercury in the gas was analyzed using a mercury analyzer (CVAAS SG-921).

At the beginning of each test, the gas containing elemental mercury first passed through the bypass without catalyst, and then entered the CVAAS to determine the baseline. When the concentration of elemental mercury became stable (fluctuated within ±5%) for more than 30 min, the gas was passed through the fixed-bed reactor with the catalyst. Until the adsorption of Hg⁰ on the catalyst was saturated, 5 ppm HCl was passed to estimate the oxidation efficiency of Hg⁰, and when the concentration of elemental mercury became stable for more than 30 min, the oxidation efficiency was collected. The Ontario Hydro Method (OHM) was used to test the balance of mercury before and after the conversion. The OHM sample analysis and the adsorbed mercury on the catalyst were determined by a RA-915⁺ mercury analyzer (Lumex, Russia) equipped with a liquid analysis unit and a solid pyrolysis unit (RP-91C), respectively.²⁷ The flow rate of the simulative gas, which used nitrogen as a carrier gas, was 500 ml min⁻¹, and the oxygen content was set at 4%.

2.4 Characterization of the catalysts

The XRD patterns of the catalysts were obtained by an X-ray diffractometer (APLX-DUO, BRUKER, Germany) using Cu Kα radiation (40 kV and 20 mA). The microstructures of the catalysts were analyzed by transmission electron microscopy (TEM). The samples were dispersed in ethanol with strong sonication before the analysis. H₂-TPR experiments were performed on a Chemisorp TPx 2920 instrument, the

sorbents were degassed at 200 °C for 3 h under Ar at atmosphere before the H₂-TPR test, and the reducing gas was 10% H₂/Ar. The X-ray photoelectron spectroscopy (XPS) measurements were done with an AXIS Ultra DLD (Shimadzu-Kratos) spectrometer with Al K α as the excitation source. The C 1s line at 284.8 eV was taken as a reference for the binding energy calibration. Nitrogen adsorption and desorption isotherms were obtained on nitrogen-adsorption apparatus (Quantachrome Nova 2200e) at -196 °C (temperature of the liquid nitrogen bath). All samples were degassed for 3 h at 200 °C before testing. Specific surface areas were calculated by use of the Brunauer-Emmett-Teller (BET) method.

3. Results and discussion

3.1 The effect of silver on the catalytic oxidation of Hg⁰

Fig. 1 shows the comparison of the Hg⁰ catalytic oxidation efficiencies over V-Ti and Ag-V-Ti at various temperatures

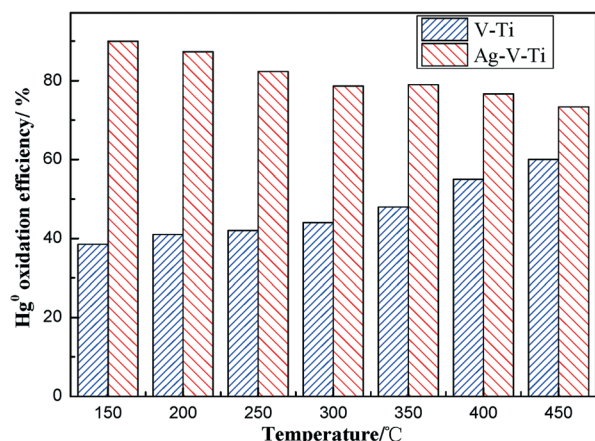


Fig. 1 The effect of silver on the catalytic oxidation of Hg⁰.

and a space velocity of $4.26 \times 10^5 \text{ h}^{-1}$. As can be seen from Fig. 1, the catalytic efficiency of V-Ti was improved with the increase of temperature, while the Hg⁰ catalytic oxidation capacity of Ag-V-Ti was slightly reduced with the increasing temperature, which indicated that the properties of V-Ti and Ag-V-Ti were different. In addition, the Hg⁰ oxidation capacity of Ag-V-Ti was higher than that of V-Ti regardless of whether it was at low or high temperature. This indicated that adding silver was beneficial for the catalytic performance of the V-Ti catalyst. As a result, it was necessary to prepare well distributed silver nanoparticles on the carrier and analyze the physical and chemical properties of the catalysts and the reaction mechanism.

3.2 The physical and chemical properties of the catalysts

Fig. 2 shows the transmission electron microscopy (TEM) and EDS analysis of V(2%)-Ti and Ag(2%)-Ti. It can be seen from Fig. 2(a) that the V(2%)-Ti catalyst consisted of nanoparticles with sizes between 20 and 40 nm. The EDS analysis in Fig. 2(a) and the element content of V(2%)-Ti in Table 1 prove the existence of vanadic oxide on the carrier. However,

Table 1 The element content of V(2%)-Ti and Ag(2%)-Ti by EDS analysis

	Element	Weight%	Atomic%
V(2%)-Ti	O K	45.61	71.59
	Ti K	51.15	26.81
	V K	3.24	1.60
	Totals	100.00	
Ag(2%)-Ti	O K	36.37	63.47
	Ti K	61.91	36.08
	Ag K	1.72	0.44
	Totals	100.00	

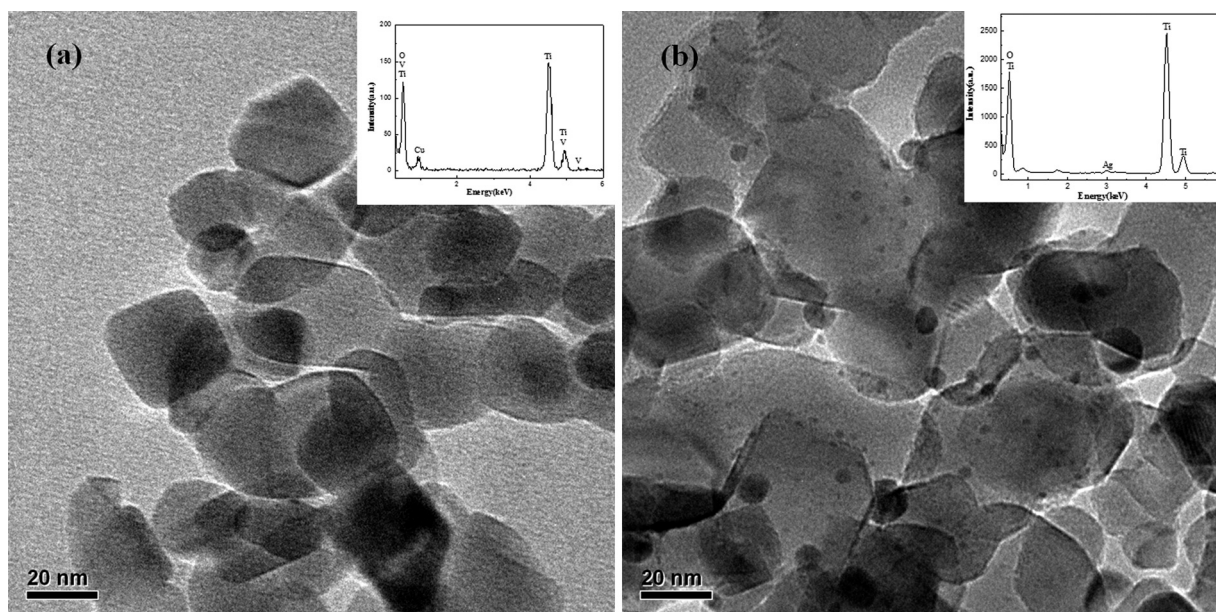


Fig. 2 TEM and EDS analysis of V(2%)-Ti (a) and Ag(2%)-Ti (b).

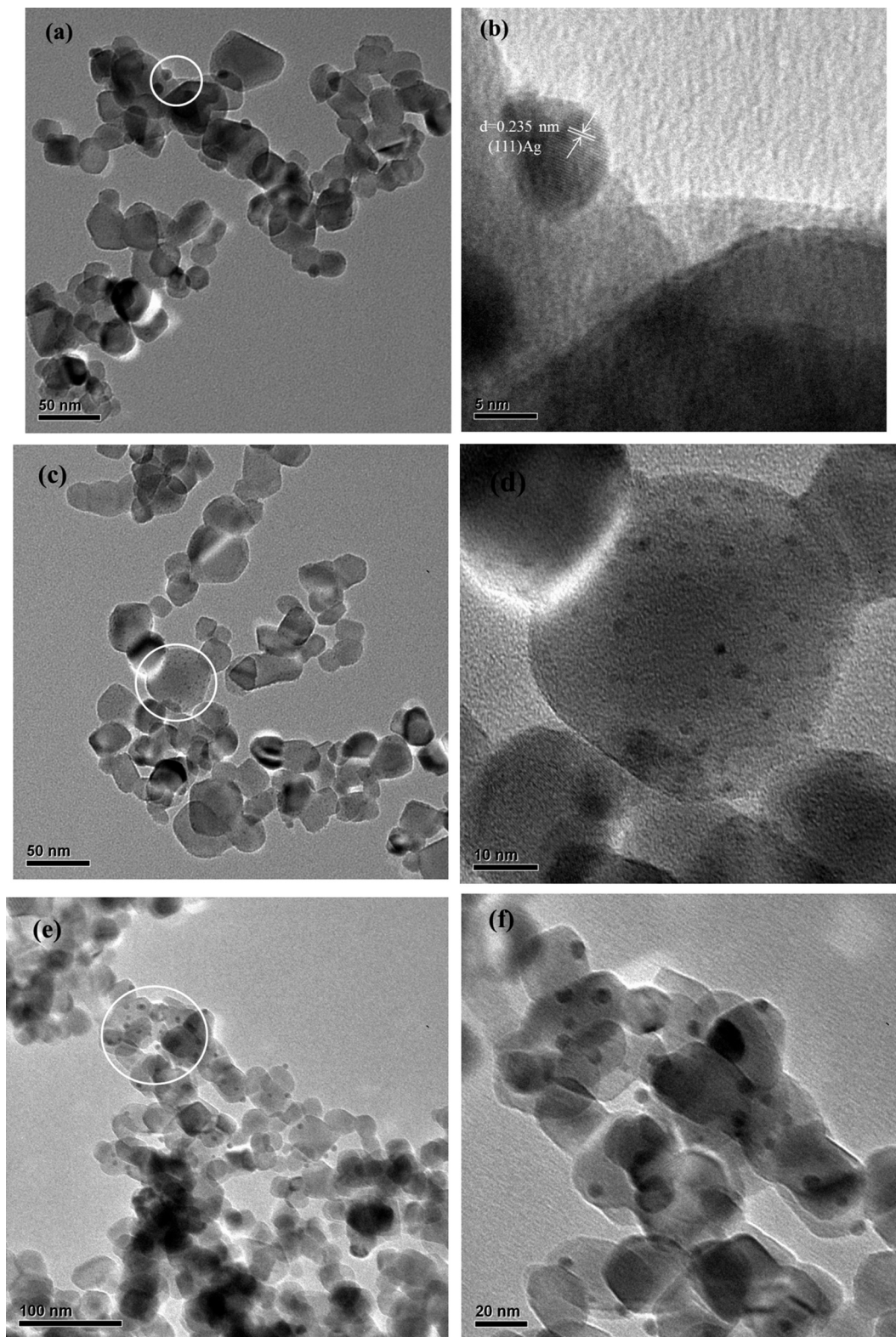


Fig. 3 TEM and HRTEM images of Ag(1%)-V(1%)-Ti (a, b), Ag(1%)-V(1%)-Ti(PVP) (c, d) and Ag(1%)-V(1%)-Ti(IL) (e, f).

vanadium oxide particles were not found on the surface of the catalyst, which indicated that the vanadium atoms were well dispersed on the TiO_2 , or even inserted into the lattice of TiO_2 .

Fig. 2b shows the transmission electron microscopy (TEM) analysis of Ag(2%)-Ti. It can be seen that there existed many small particles attached on the surface of the TiO_2 , which could be Ag nanoparticles from the EDS analysis in Fig. 2(b)

and the element content of Ag(2%)-Ti in Table 1. The sizes of these particles ranged from 1 to 10 nm. It was believed that the silver ions deposited on the TiO₂ nanoparticles were reduced to Ag⁰ species through the calcination, and the newly formed Ag⁰ species with small size were unstable and could further agglomerate to form larger Ag⁰ particles due to the lack of the necessary barrier to the mobility of tiny particles.²⁸

Fig. 3 shows the transmission electron microscopy (TEM) analysis of Ag(1%)-V-Ti, Ag(1%)-V(1%)-Ti(PVP) and Ag(1%)-V(1%)-Ti(IL). It can be seen that there existed small and large particles on the TiO₂ in Fig. 3(a), which indicated that Ag⁰ species were successfully deposited onto the carriers. However, the sizes of the silver nanoparticles were irregular and the nanoparticles were widely distributed. The HRTEM image in Fig. 3(b) corresponding to the circled area in Fig. 3(a) shows the crystal lattices with distances of 0.235 nm, which can be attributed to cubic Ag (1 1 1) species to further prove the existence of silver nanoparticles.²⁹

In addition, the silver nanoparticles appeared to be more evenly deposited on the titanium dioxide when PVP was used as the additive, as shown in Fig. 3(c) and (d). This indicated that the presence of PVP was important to the size of the silver nanoparticles, which was because the PVP could act as a reductant to reduce AgNO₃ to Ag nanoparticles, and then the formed Ag⁰ species with a small size tended to be anchored on the TiO₂ surfaces to reduce their surface energy. Besides, the growth of the Ag nanoparticles was inhibited due to steric effects.^{23,30} PVP could also prevent the aggregation of the Ag nanoparticles when the catalysts were calcined due to the effect of isolation and stability by PVP before decomposition.

The TEM images of Ag-V-Ti(IL) are also shown in Fig. 3(e) and (f). It can be observed that silver particles were evenly anchored on the titanium dioxide when [bmim][BF₄] was used. The size of the silver nanoparticles was about 6–7 nm, and there were no smaller silver nanoparticles presented. This indicated that silver nanoparticles can also be well dispersed with a protective layer of ionic liquid. This might be attributed to the fact that silver ions coated by ionic liquid gathered to form silver nanoparticles once calcined, and the silver nanoparticles also did not further agglomerate because of the dispersant effect of the ionic liquid.

Fig. 4 presents the XRD patterns of various catalysts calcined at 500 °C. The anatase phase and the rutile phase of TiO₂ could be clearly seen in all the catalysts in Fig. 4. The crystal type of titania was almost rutile for Ag(5%)-V(5%)-Ti when no other components were added. Some studies have demonstrated that Ag dopants promote the anatase to rutile phase transformation.³¹ However, when PVP and ionic liquid were added, the trend of phase transformation was inhibited to a certain extent, and the effect of [bmim][BF₄] was better. It may be that the reaction additives changed the size and type of silver nanoparticles. For the ionic liquid [bmim][BF₄], the size of the silver nanoparticles was large and they had little effect on the phase transformation, which could be proven by the TEM results. Because smaller silver nanoparticles and Ag⁺ can insert into the lattice of TiO₂, they can

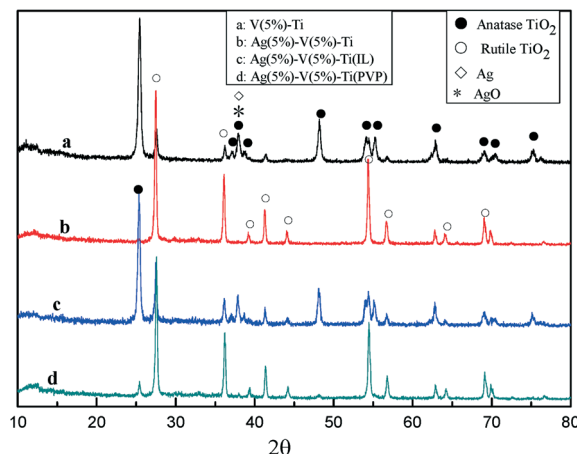


Fig. 4 XRD patterns of various catalysts calcined at 500 °C.

promote the anatase to rutile phase transformation. PVP could change the Ag⁺ ion into Ag⁰ early, so it could reduce the trend of phase transformation. Additionally, no noticeable peaks of silver oxide or silver metal were observed in the X-ray diffractograms, perhaps due to the microscale amount of Ag-doping or because the strongest peak from Ag (1 1 1) overlapped with that of anatase (0 0 4).³² There were also no characteristic V₂O₅ peaks, because the vanadium atoms were well dispersed on the TiO₂ or due to the low content, which was consistent with the TEM results.

The TPR profiles of the various catalysts are shown in Fig. 5. There was a reduction peak at about 450 °C in Fig. 5(a), which could be attributed to the typical reduction peak of dispersed vanadium oxide. This peak was lower than the reduction peak of bulk vanadium oxide, which consists of four peaks at 678, 728, 856, and 982 °C, corresponding to the following sequential reductions: V₂O₅ → V₆O₁₃ → V₂O₄ → V₆O₁₁ → V₂O₃.³³ It might be that it is was the interaction between vanadium oxide and TiO₂ that made the reduction temperature of vanadium decrease, on the basis of the TEM and XRD results.

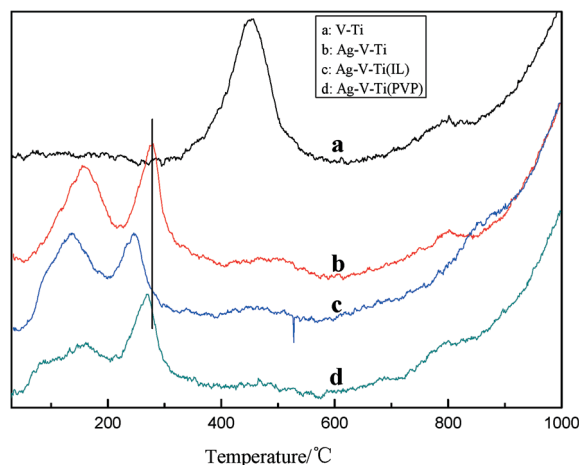


Fig. 5 TPR profiles of the various catalysts: V-Ti (a), Ag-V-Ti (b), Ag-V-Ti(IL) (c), Ag-V-Ti(PVP) (d).

Fig. 5(b) shows two reduction peaks. The peak at about 150 °C was assigned to the reduction of Ag_2O ,³⁴ and the peak at about 280 °C could be assigned to the reduction peak of dispersed vanadium oxide, which was shifted to a lower temperature compared with V-Ti in Fig. 5(a). It might be that the bond strength of $\text{V}=\text{O}$ was weakened and the activation energy values of desorption for the surface oxygen species decreased explicitly due to the activation effect of silver and hydrogen overflow.³⁵

It can also be seen from Fig. 5(c) and (d) that the reduction peaks of Ag_2O and vanadium oxide all further shifted to lower temperatures compared with Fig. 5(b). This might be due to the larger size of silver nanoparticles for Ag-V-Ti(IL) or the larger proportion of Ag^0 for A-V-Ti(PVP), which made it easier to produce active hydrogen and hydrogen overflow.

Fig. 6 illustrates the XPS spectra of V-Ti, Ag-V-Ti(IL) and Ag-V-Ti(PVP) over the spectral regions of V 2p and Ag 3d. As can be seen from Fig. 6(a), there were three peaks of V 2p.

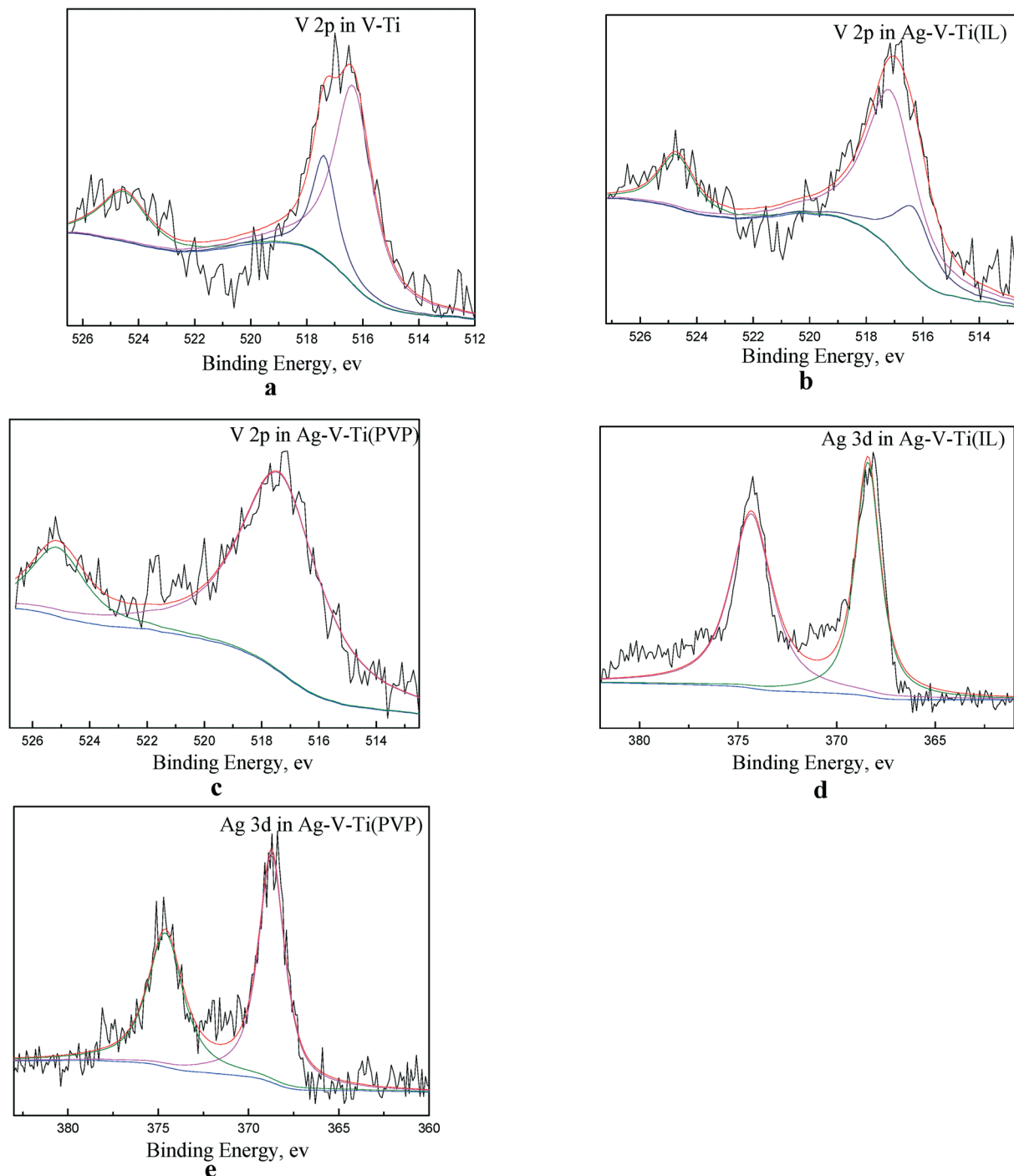


Fig. 6 XPS spectra of V-Ti, Ag-V-Ti(IL) and Ag-V-Ti(PVP) over the spectral regions of V 2p and Ag 3d.

The peak located at about 516.2 eV was attributed to V^{4+} of the V 2p_{3/2} electronic state, and the peaks at about 517.3 and 524.5 eV could be assigned to V^{5+} 2p_{3/2} and V^{5+} 2p_{1/2}.³⁶ The peaks of V 2p could also be seen in Fig. 6(b) and (c), in which the difference was the proportion of V^{5+} . The Ag-V-Ti(IL) and Ag-V-Ti(PVP) had a higher proportion of V^{5+} . This indicated that adding silver to V₂O₅/TiO₂ could induce a higher oxidation state of the vanadium, and a higher oxidation state of vanadium could induce better catalytic performance owing to the Mars and Van Krevelen mechanism,¹⁵ which meant that Ag-V-Ti(IL) and Ag-V-Ti(PVP) had a higher mercury oxidation efficiency than V-Ti.

It has been reported that the binding energies of Ag 3d_{5/2} for Ag, Ag₂O and AgO are 368.4, 367.7, and 367.4 eV, respectively.³⁷ The XPS peaks of Ag 3d in Fig. 6(d) and (e) clearly showed that silver was mostly present in the metallic state, which indicated that the particles on the V₂O₅/TiO₂ were silver nanoparticles, as suggested by the TEM results.

3.3 Catalyst activity

Fig. 7 shows the Hg⁰ catalytic oxidation efficiencies of the various catalysts at 350 °C. As can be seen from Fig. 7, both V-Ti and Ag-Ti had a certain ability to oxidise mercury, but it was not high. When the V and Ag components were combined, it could significantly improve the catalytic activity, which might be due to a synergism operating between the Ag, V and Ti, and the higher proportion of V^{5+} as shown by the XPS results. It can also be seen from Fig. 7 that the catalytic efficiency of Ag-V-Ti(IL) was lower than that of Ag-V-Ti, which might be due to the small specific surface area, due to the larger silver particles. This can be proven by the results shown in Table 2, which show that the BET specific surface areas of the catalysts made by adding silver were larger than that of V-Ti, except for Ag-V-Ti(IL), and the high specific surface area was beneficial for the catalytic reaction. Ag-V-Ti(PVP) had the highest catalytic efficiency. Besides, the catalytic efficiency of Ag-Ti(PVP) was higher than

Table 2 The BET specific surface areas of the various catalysts

Catalyst	BET (m ² g ⁻¹)
V-Ti	39.457
A-V-Ti	50.708
A-V-Ti(IL)	38.31
A-V-Ti(PVP)	47.211

that of Ag-Ti, which was due to the smaller silver particles and uniform dispersion, on the basis of the TEM results.

The Hg⁰ catalytic oxidation efficiencies of Ag-V-Ti(PVP) under various conditions are shown in Fig. 8. The catalytic efficiency was high in the presence of HCl, whether at low or high temperature, which indicated that the temperature window of Ag-V-Ti(PVP) was wide. It might be that the formation of silver amalgam at low temperature and the interaction of amalgamate Hg⁰ with adsorbed HCl to form a Hg-chloride intermediate is a prelude to the formation of HgCl₂.³⁸ In addition, the oxidation ability of V was improved by adding silver due to the higher proportion of V^{5+} and the redox temperature of the catalyst was lowered owing to the weakened bond strength of V=O. With the increase of temperature, the amalgamation effect of silver to mercury became weak, which induced a slightly downward trend of the Hg⁰ catalytic oxidation efficiency. Meanwhile, the oxidation ability of V-Ti was enhanced with increasing temperature, as shown in Fig. 1, and silver could decrease the apparent activation energy of the various reactions,³⁹ so the production of active chlorine atoms and chlorine, which could react with gaseous mercury, would increase with the increasing temperature. Therefore, the Hg⁰ catalytic oxidation efficiency increased slightly again. Above 400 °C, the catalytic oxidation efficiency of Hg⁰ began to significantly decrease, which indicated that the high temperature was bad for the catalytic activity. It may be that the adsorption capacity and catalytic performance of Ag-V-Ti might be poor at high temperature, and the activation energy of oxidizing Hg⁰ by direct

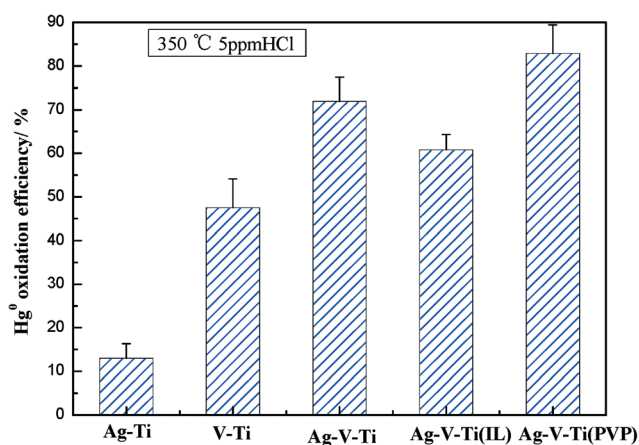


Fig. 7 Comparison of the Hg⁰ catalytic oxidation efficiencies over various catalysts with 5 ppm HCl at 4.26×10^5 h⁻¹ space velocity.

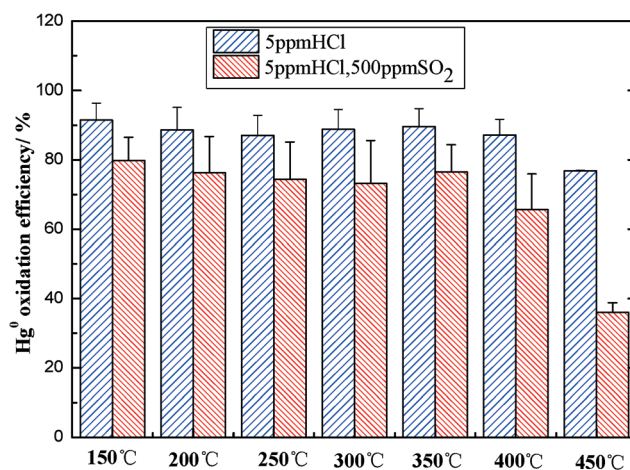


Fig. 8 The Hg⁰ catalytic oxidation efficiencies of Ag-V-Ti(PVP) under various conditions at 4.26×10^5 h⁻¹ space velocity.

gas phase oxidation was higher than that over the catalyst.⁶ It manifested that the low temperature and the middle temperature were more suitable. When sulfur dioxide was added, the catalytic efficiency began to fall at any temperature, which might be because SO_2 competed for the active sites to inhibit the reaction of Hg^0 and Cl . However, the catalytic efficiencies were still high, which showed that the catalyst had a certain ability to resist sulfur.

Fig. 9 shows the Hg^0 catalytic oxidation efficiencies of Ag–V–Ti(PVP) with various space velocities (SV) at 350 °C. It was clearly observed that the Hg^0 catalytic oxidation efficiencies were gradually increased with the decrease of space velocity, no matter whether 5 ppm HCl or a mixture of 5 ppm HCl and 500 ppm SO_2 was present. This might be because the residence time of the simulated flue gas was longer at lower space velocity, which meant a longer reaction time between the flue gas and the catalyst. It also suggested that SO_2 had a slight inhibition effect on the Hg^0 catalytic oxidation efficiency at different space velocities, and when the SV was under $2.84 \times 10^5 \text{ h}^{-1}$, the Hg^0 catalytic oxidation efficiencies can reach above 80%, even in the presence of SO_2 . During the actual operation, choosing a corresponding space velocity to reach a certain catalytic efficiency was necessary.

To make the role of silver clear, Ag was loaded onto an inert Ti catalyst, and experiments of Ag–Ti(PVP) with HCl present and with no HCl present were performed. Fig. 10 shows the Hg^0 catalytic oxidation efficiencies of Ag–Ti with adsorption and 5 ppm HCl. It can be seen from Fig. 10 that the adsorption capacity of Ag–Ti was higher at low temperature than at high temperature, and it was indicated that some silver amalgam was formed. When 5 ppm HCl was added, the Hg^0 catalytic oxidation efficiencies were improved, and had a trend of reducing firstly and then increasing with increasing temperature. This indicated that HCl could be adsorbed on the surface of Ag–Ti(PVP), which reacted with the Hg^0 in the silver amalgam. The adsorption capacity of Ag–Ti(PVP) was weakened with increasing temperature, so

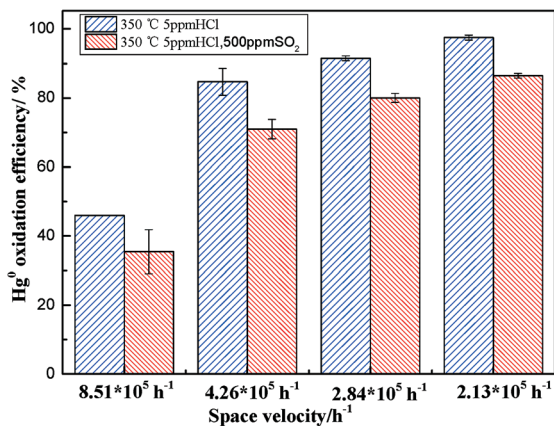


Fig. 9 The Hg^0 catalytic oxidation efficiencies of Ag–V–Ti(PVP) at various space velocities (SV).

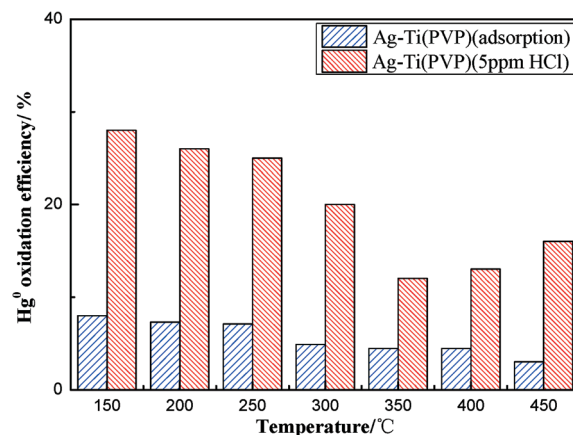


Fig. 10 The Hg^0 catalytic oxidation efficiencies of Ag–Ti(PVP) with adsorption and 5 ppm HCl.

the Hg^0 catalytic oxidation efficiency was reduced. However, the activity of the catalyst was enhanced at high temperature, and production of active chlorine atoms and chlorine would increase, so the catalytic oxidation efficiency of Hg^0 was improved. Based on the above, Ag acted in both absorption and catalysis roles by itself, and adding silver into V–Ti catalysts can enhance the adsorption ability of the catalyst, and induce a higher oxidation state of the vanadium to improve the oxidation ability of the catalyst.

4. Conclusions

Catalysts were prepared successfully by an impregnation method with different additives, and silver nanoparticles were loaded onto the carrier and were well dispersed by adding PVP or [bmim][BF₄] ionic liquid. The size of the silver nanoparticles of Ag–V–Ti(II) was larger than that of Ag–V–Ti(PVP). The silver was mostly present as zero-oxidation silver (Ag^0). In addition, silver could weaken the strength of $\text{V}=\text{O}$ and decrease the activation energy values of desorption of surface oxygen species. Adding silver can induce a higher oxidation state of the vanadium, so it could increase the oxidation ability of the catalyst and lower the redox temperature. The experiments of Hg^0 catalytic oxidation indicated that doping silver on the V–Ti catalyst could significantly improve the performance of the catalyst. The Hg^0 catalysis mechanism might be that amalgamate Hg^0 and adsorbed Hg^0 interact with adsorbed HCl to form a Hg–chloride intermediate in prelude to the formation of HgCl_2 at low temperature, and active chlorine atoms or chlorine catalyzed by the catalyst reacted with gaseous mercury at high temperature. All these factors were good for the oxidation of mercury. Ag–V–Ti(PVP) had the highest catalytic efficiency and had a wide temperature window. This was due to the small metallic silver nanoparticles and their uniform dispersion, which was good for the synergism that operates between the Ag, V and Ti. In addition, sulfur dioxide slightly inhibited the Hg^0 oxidation.

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