Photocatalytic performance of TiO$_2$ catalysts modified by H$_3$PW$_{12}$O$_{40}$, ZrO$_2$ and CeO$_2$

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Abstract

The binary composite photo-catalysts CeO$_2$/TiO$_2$, ZrO$_2$/TiO$_2$ and the ternary composite photo-catalysts H$_3$PW$_{12}$O$_{40}$-CeO$_2$/TiO$_2$, H$_3$PW$_{12}$O$_{40}$-ZrO$_2$/TiO$_2$ were prepared by sol-gel method. The catalysts were characterized by thermogravimetric-differential thermal analysis (TG-DTA), scanning electron microscopy (SEM) and X-ray diffraction (XRD). The photocatalytic elimination of methanol was used as model reaction to evaluate the photocatalytic activity of the composite catalysts under ultraviolet light irradiation. The effects of doped content, activation temperature, time, initial concentration of methanol and gas flow rate on the catalytic activity were investigated. The results showed that after doping a certain amount of CeO$_2$ and ZrO$_2$, the catalytic oxidation of methanol was restrained, particles of catalysts are smaller and more uniform. Doping ZrO$_2$ not only significantly improved the catalytic activity, but also increased thermal stability. Doping H$_3$PW$_{12}$O$_{40}$ also enhanced the catalytic activity. The catalytic activities of binary and ternary composite photocatalysts were significantly higher than un-doped TiO$_2$. The dynamics law of photocatalytic reaction over the binary CeO$_2$/TiO$_2$ and ZrO$_2$/TiO$_2$ catalysts has been studied. The activation energy 15.627 and 15.631 kJ/mol and pre-exponential factors 0.5176 and 0.9899 s$^{-1}$ over each corresponding catalyst were obtained. This reaction accords to the first order dynamics law.

Key words: TiO$_2$; H$_3$PW$_{12}$O$_{40}$; ZrO$_2$; CeO$_2$; photocatalytic elimination of methanol

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Introduction

In recent years, water treatment, air purification, sunlight utilization are very active research topics in photo-chemistry field, in which TiO$_2$ plays an important role (Alisafarzadeh and James, 1996; Yamashita et al., 1996; Regan et al., 1991; Tetsuto et al., 2003). However, the utilization of pure TiO$_2$ is constrained because of its wide band gap, low efficiency of sunlight utilization due to its need in ultraviolet range, low quantum efficiency and high recombination rate of electrons-holes. Therefore, TiO$_2$ needs to be modified by doping other element to reduce its wide band gap and extend the optical absorption range to long wavelength. By reducing the recombination rate of electrons-holes, decreasing TiO$_2$ grain size and increasing specific surface area of TiO$_2$, the photo-catalytic activity can be enhanced (Wu et al., 2004).

Nano-sized ZrO$_2$ is an inorganic material with extensive application and unique properties (Lindén et al., 1999; Lombard et al., 1989). Yang and Ferreira (1998) also found that doping with a certain amount of Zr could improve the surface area of TiO$_2$ powder. Meanwhile, they found that the augment of the surface area could increase the ability of surface to adsorb O$_2$ and –OH, and then increase the opportunity to accept electron. Over catalyst doped with Zr, some Zr$^{4+}$ are adsorbed on the particle surface, which boosts the surface potential to certain extent, and helps the free electrons diffuse from the interior to the surface, improving the photo-catalytic activity of catalyst.

The rare earth oxide CeO$_2$ is broadly used in luminous materials, polishing powder, electronic ceramics, and used as efficient catalyst in photo-catalytic field (Aguiar et al., 2002). The oxygen ion with fast diffusion rate in the crystal lattice of CeO$_2$ can exchange equivalently with oxygen molecules outside. The number of this kind of oxides is very few. Variable valences of Ce such as Ce$^{4+}$ and Ce$^{3+}$ improve characteristics of CeO$_2$ in transferring electrons and enhance the light absorption capability in near ultraviolet or ultraviolet. Meanwhile, doping with CeO$_2$ can double oxygen reserve and transfer capacity of the catalyst, which greatly improves the catalytic oxidation activity.

Heteropoly compounds have the unique property of structural stability, strong acidity and strong oxidation activity. It is applied widely in the catalyst field (Hill and Prosser-McCartha, 1995; Mizuno and Misono, 1998; Kozhevnikov, 1998; Deng et al., 2005), such as in photo-
catalysis reaction (Hori et al., 2003, 2004; Gkika et al., 2006). The photocatalysis of heteropoly compound study performed by our group indicates that $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2$ (Deng et al., 2005), $\text{NdPW}_{12}\text{O}_{40}/\text{TiO}_2$ (Cai et al., 2007), $\text{BiPW}_{12}\text{O}_{40}$ (Wu et al., 2008), $\text{Cu}_3(\text{PW}_{12}\text{O}_{40})_2$ (Deng et al., 2007) had high photocatalytic activities in photocatalytic elimination of formaldehyde, acetone, methanol, and so on.

This article reported the binary and the ternary composite photocatalysts, which were prepared by modifying $\text{TiO}_2$ with $\text{CeO}_2$, $\text{ZrO}_2$ and $\text{H}_3\text{PW}_{12}\text{O}_{40}$ using sol-gel method. We expected to find some synergy between the multiple components in each prepared photocatalysts to enhance the catalytic activity. The photo-catalytic elimination of methanol was used as model reaction to evaluate the photocatalytic activity. The dynamics law of photocatalytic elimination of methanol over the binary composite photocatalyst was also studied.

1 Materials and methods

1.1 Catalyst preparation

All chemicals are of analytical reagent grade. A certain amount of $\text{Ti(Obu)}_4$ (chemical pure) was dissolved in anhydrous ethanol while quickly stirring, obtaining the solution A. Then solution B, a mixture of anhydrous ethanol, distilled water and acetic acid, was added dropwise to solution A under stirring. Then a transparent solution was obtained. After continuous stirring for 2 h, a milky wet gelatin was formed. After aging for 24 h at room temperature, the gelatin was dried at microwave oven followed by grinding and baking to obtain $\text{TiO}_2$ photocatalyst, denoted as 1#.

Using similar method except for adding a given mount of $\text{ZrOCl}_2$ or $(\text{NH}_3)_2\text{Ce(NO}_3)_3$ to solution B, $\text{ZrO}_2/\text{TiO}_2$ and $\text{CeO}_2/\text{TiO}_2$ were prepared, denoted as 2# and 3#, respectively. $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{ZrO}_2/\text{TiO}_2$ and $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{CeO}_2/\text{TiO}_2$ were prepared according to the same way as 2# and 3# with the addition of certain amount of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ to solution A, denoted as 4# and 5#, respectively.

All the catalysts must be activated at different temperatures of different time before being used in the photocatalytic reaction. The temperature varies from 350 to 600°C, and the time varies from 1.5 to 4.0 h.

1.2 Catalyst characterization

The morphology of the catalysts were observed by scanning electron microscopy (SEM) using a Sirion 200 auto emission scanning electron microscope (FEI Co., Holland, working voltage of 5 kV). Thermogravimetric-differential thermal analysis (TG-DTA) was carried out on a WCT-1A microcomputer differential thermal balance (Beijing Optical Instrument Factory, China) in air atmosphere with a heating rate of 10°C/min. X-ray diffraction (XRD) was performed on a Rigaku D/Max 2500 PC X-ray diffract meter using Cu $K_\alpha$ radiation ($\lambda = 0.154056$ nm).

1.3 Photocatalytic reaction for methanol elimination

The photocatalytic activity tests were performed in a home-made continuous flow photo-catalytic tube reactor with an inner diameter of 6.0 mm and length of 260 mm. Two 8 W UV lamps ($\lambda = 254$ nm) were used as light source. The catalyst loading was 0.1 g. The model polluted air containing methanol was prepared by bubbling clean air into a container filled with methanol solution, passing the gas through anhydrous CaCl$_2$, and diluting the gas with clean dry air. The initial concentration of the reaction gas was 0.1 g/L. The model polluted air was controlled by changing the proportion of the bubbling gas and diluent gas.

The concentration of products was determined every 20 min by an online GC-9800 gas chromatograph equipped with a Porapak-Q column and flame ionization detector (FID) (Shanghai, China). The inorganic products CO and CO$_2$ were monitored with the 0.2% PdCl$_2$ solution and saturated limewater, respectively. The UV lamps were not turned on until the concentration of the feed gas was stable. The blank experiments were carried out under ultraviolet light only (no catalyst) and catalyst only (no ultraviolet light irradiation) conditions.

The photocatalytic reaction was carried at 40°C, exclude dynamics determination experiment of different temperatures.

2 Results and discussion

2.1 Characterization of catalysts

2.1.1 Thermogravimetric-differential thermal analysis

The TG-DTA curves of the catalysts 1#, 2# and 3# are shown in Fig. 1. The curves at low temperatures were similar. In the temperature range 40–80°C, a weak endothermic peak appeared, indicating the loss of water and alcohol. The peaks of 2# and 3# were weaker than that of 1#.
which indicated that the contents of water and alcohol in dry gel 2# and 3# were less than that in pure TiO2. This meant that the particles of catalysts do not agglomerate easily in the later processing. At high temperature region, there was a sharp exothermic peak around 346°C for 1#, meanwhile, for 2# and 3# the exothermic peaks are obviously broadened and became more flat, extending from 273°C to the vicinity of 500°C. Therefore, it can be concluded that for TiO2 doped with CeO2 or ZrO2, phase transitions (from amorphous to anatase) occurred slowly at lower temperature, which helps to heighten the degree of anatase and obtain more integrated and uniform crystal.

2.1.2 Scanning electron microscopy

The SEM micrographs of the catalysts 1#, 2# and 3# are shown in Fig. 2. The particle sizes of 2# and 3# were smaller and more even than that of 1#. The surface of pure TiO2 presented agglomerated congeries with non-slippy surface and uneven particle, the particle size of 1# was 25–40 nm. After doping with a certain amount of CeO2 or ZrO2, the morphology of 2# and 3# presented obvious change, the surface of these catalyst became more slippery. Interspaces of particles and agglomeration were reduced. Particle size was more uniform and dwindled to 15–25 nm. ZrO2 prevented TiO2 particles agglomeration more markedly and smaller. There may be strong interactions, which are beneficial to the activity of the catalysts, between each component including restraining crystallization process of TiO2, interfering with the growth of crystal particles, inhibiting the aggregation of TiO2 particles, and augmenting the surface. The experimental results agreed with the characterizations, that is, the catalysts doped with a certain amount of CeO2 or ZrO2 were more active than pure TiO2.

2.1.3 X-ray diffraction

The XRD patterns of the catalysts 2#, 3#, and anatase TiO2 are shown in Fig. 3. The XRD patterns of 3# is similar to that of 2#. The 2# sample activated at 500°C for 2.5 h exhibited diffraction peaks of anatase phase and no diffraction peaks of rutile phase and ZrO2, which indicated that TiO2 in 2# was anatase phase. Compared to pure TiO2, the TiO2 characteristic peak of 2# has not shifted either. Ti and Zr are the same group elements, and both are quadrivalence ions with similar ionic radius. Therefore, Zr4+ is able to enter into the crystal lattice of TiO2 easily. However, no characteristic peak of ZrO2 and the shift of TiO2 characteristic peak of 2# were observed. The possible reason may be that ZrO2 doping is small and ZrO2 was highly scattered over TiO2. After activating at 450°C, pure TiO2 began to phase transfer from anatase phase to rutile phase. The phase transition temperature increased above 500°C after doping with ZrO2, which showed that ZrO2 slowed down phase transition rate, thereby improved the
thermal stability of low temperature anatase phase.

The 3# sample activated at 450°C for 3 h exhibited diffraction peaks of anatase phase. Without diffraction, peak of rutile phase and CeO$_2$ cerianite phase indicated that TiO$_2$ in 3# catalyst was also anatase phase. Compared with pure TiO$_2$, the TiO$_2$ characteristic peak of 3# has not changed, which indicated that Ce$^{4+}$ has not substituted for Ti$^{4+}$. The reason may be that the radius of Ce$^{4+}$ is 0.0993 nm, which is much larger than Ti$^{4+}$ radius of 0.0680 nm (Xu et al., 2002). Therefore, Ti$^{4+}$ may enter into CeO$_2$ lattice and form solid solution. Because the entering of Ti$^{4+}$ into CeO$_2$ lattice may change the crystal structure of CeO$_2$ and CeO$_2$ may be highly dispersed on the TiO$_2$ surface, CeO$_2$ cannot form the cerianite phase. The diffraction peaks of CeO$_2$ cerianite phase is not found either.

Comparing with the standard spectra, the sample exhibited diffraction of the anatase phase (101 crystal plane), according to Scherrer equation (Eq. (1)).

\[
D = \frac{R_0}{\beta \cos\theta}
\]

where, \(D\) is particle diameter, \(R\) is Scherrer constant (0.89), \(\lambda\) is the wavelength of the X-ray (0.15406 nm), \(\theta\) (°) is the diffraction angle, \(\beta\) (rad) is the line width at half maximum height, the average particle diameter of anatase phase in 2# and 3# calculated is about 8.0 nm. The average particle diameter calculated according to Scherrer equation is the distance between the two crystal surfaces, while it is a secondary grain piled up from a number of grain in the SEM, therefore, they are different (Liu and Liu, 2005).

2.2 Photocatalytic elimination of methanol

The blank experiments showed that methanol in the model polluted air was hardly eliminated either under ultraviolet irradiation without catalyst or over catalyst without ultraviolet irradiation. Thus, the photocatalytic elimination of methanol was tested over the catalysts under ultraviolet irradiation. From the GC analysis results, there is no new peak in GC spectra after the photocatalytic reaction. The saturated limewater changed to white and the color of 0.2% PdCl$_2$ solution did not change, indicating that there are CO$_2$ but not CO. Products of elimination of methanol were CO$_2$ and H$_2$O.

2.2.1 Effect of doping content

Doping content can influence the thickness of the superficial space-charge layer of TiO$_2$, the best thickness is about 2 nm, which decreases with increasing amount of dopant ions. Only when the space-charge layer thickness approximates the penetration depth of light into the solid, all electron-hole pairs can be effectively separated (Liu and Liu, 2005).

The photocatalytic elimination of methanol with initial concentration 10.0 g/m$^3$ and flow rate 7 mL/min over the 0.1 g catalysts doped with different amounts of CeO$_2$ or ZrO$_2$ was tested. As shown in Fig. 4a, there existed an optimum doping content. When doping content was low, increasing its concentration can increase trapping sites of carriers, improve separation effect of photo-generated electrons and holes, which can prolong the lifetime of carriers, thereby to improve the photocatalytic activity. However, when the doping concentration exceeded a certain amount, photo-generated charge carriers may lose activity easily after repeatedly captured over the impurity site. The dopant ions acted as recombination centers of electrons and holes, which was not conducive for the carriers transferring to the interface. High concentration doping can decrease the surface space-charge layer thickness of TiO$_2$ particles and reduce the photon absorption (Liu et al., 2001). It would also affect the adsorption performance of –OH in the particle surface and decrease photo-catalytic activity (Martra, 2000). Therefore, low concentration doping is beneficial to the reaction, while high concentration doping reduce the photocatalytic activity. The optimum contents of CeO$_2$ and ZrO$_2$ were 0.04 wt.% and 0.2 wt.%, respectively.

On the basis of the optimum content of CeO$_2$ or ZrO$_2$, the photo-catalytic activity of catalysts doped with different contents of H$_3$PW$_{12}$O$_{40}$ for methanol elimination is shown in Fig. 4b. The optimum content of H$_3$PW$_{12}$O$_{40}$ in both catalysts was 0.6 wt.% and 1.0 wt.%, respectively.
2.2.2 Effect of activation temperature and activation time

The catalysts were activated at different temperatures in muffle oven. The effect of activation temperature on the photocatalytic elimination of methanol over catalysts is shown in Fig. 5a. It is found that with the increase of activation temperature, the elimination rate of methanol increased first, and then decreased over the catalysts 1#, 3# and 5#. These catalysts activated at 450°C had the best catalytic activity. The catalytic activities of 3# and 5# were higher than that of 1#, because of the doping of CeO2 and H3PW12O40. TiO2 as the main catalyst component, its crystal phase transition directly affected the activity of the catalysts. Below 450°C, TiO2 could not changed from the amorphous state to anatase completely. At the same time, the organic matters added in the preparation process did not completely decomposed at lower temperature, and some organic groups form Ti–O–C polymer together with TiO2 particles, which also decreased the active sites, so its catalytic activity was relatively low. Above 450°C, anatase phase changed to rutile phase having low photocatalytic activity. As temperature increase the agglomeration phenomenon of the catalyst particulates occurred, some active sites may be destroyed, which also reduced the activity. Therefore, 450°C was selected as the optimum activation temperature of catalysts.

For catalysts 2# and 4#, similar phenomenon was observed, but 500°C was their optimum activation temperature. Adding CeO2, ZrO2 and H3PW12O40 can improve the photocatalytic activity. ZrO2 not only greatly enhanced the catalytic activity but also made TiO2 finish the phase transition of anatase in a short time. Catalysts 2#, 3#, 4#, 5# showed obviously higher activity than 1# in the same activation conditions. Among them, the activities of 4# and 5# were obviously higher than others, which implied that doping H3PW12O40 can enhance photocatalytic activity even more.

The decomposition temperature of H3PW12O40 is 588°C (Wang et al., 1984), which is higher than that in the process of preparation, activation or catalytic reaction. Therefore, the active component in catalyst should be H3PW12O40. ZrO2 and CeO2 improve the surface structure of TiO2, while H3PW12O40 of good photo-electric performance. They together raise photocatalytic activity of the matrix.

2.2.3 Effect of initial concentration and flow rate of methanol

When initial concentration of methanol was 10.2 g/m³, the results of methanol elimination with different flow rates of methanol over the 2#, 3#, 4# and 5# catalysts are shown in Fig. 6a. When the flow rate was less than 4 mL/min, the methanol can be eliminated over the four catalysts, meeting the Emission Standard. The activities of 5# and 3# were similar. The 4# catalyst showed the highest activity, when the rate flow was 5 mL/min, the elimination rate of methanol was still close to 100%. When the rate flow exceeded 7 mL/min, the elimination rate dropped to 90%. Although the elimination rate rapidly decreased with continuous increasing flow rate, the elimination rate was slightly higher than that of 2#, and their activities were all obviously higher than that of 1#.
still higher than 2# at the same flow rate.

The elimination of methanol with different initial concentrations in a flow rate of 7 mL/min over the 2#, 3#, 4# and 5# catalysts are shown in Fig. 6b. When the concentration was less than 4.8 g/m³, methanol can be totally eliminated over 3# catalyst. Over 2# catalyst, when concentration was less than 5.0 g/m³ the methanol can be completely eliminated, when the concentration was 5.5 g/m³ methanol concentration after elimination can meet the emission standard (SEPA, 1992).

The activities of 5# and 3# were similar. Over 4# catalyst, the methanol can be completely eliminated when the concentration was 5.5 g/m³. When concentration was higher than 5.5 g/m³, the elimination rate began to decline. But the elimination rate of 4# was higher than that of 2# under the same initial concentration of methanol. Evidently, the doping of the third component H₃PW₁₂O₄₀ played an important role. We can also draw the conclusion that doping of H₃PW₁₂O₄₀ enhanced the activity. Under irradiation of ultraviolet light and oxygendecondition, organic molecules may be oxidized by crystal O²⁻ in heteropoly compound ion, which is then recruited by O₂ molecules. Because of special structure, Keggin type heteropoly compound ion has strong ability as electron acceptor. When nano-sized TiO₂ was modified with heteropoly compound, electrons resulted by photo-absorption can be captured by heteropoly compound ion, which decreased the recombination rate of electron-hole pairs and increased photocatalytic efficiency of TiO₂. It can be concluded from Fig. 6 that a lower initial concentration and lower flow rate are beneficial for methanol elimination.

2.3 Study on dynamics law

The dynamics law over the binary composite catalysts was studied to understand more about photocatalytic elimination of methanol. The photocatalytic reaction usually follows first order reaction Eq. (2).

\[
k = \frac{V}{W} \ln \frac{1}{1 - x}
\]  

where, \(x\) is the conversion rate of reactant, \(k\) is the reaction rate constant at a certain temperature; \(V\) and \(W\) are the volume flow velocity of gas and the feed amount of catalyst, respectively.

When initial concentration of methanol is 10.3 g/m³, the volume flow velocity of gas is 7 mL/min and the feed amount of catalyst is 0.1 g, the conversion rate \(x\) at different temperatures can be measured. From Eq. (2) the reaction rate constant \(k\) at a certain temperature can be obtained according to Arrhenius formula (Eq. (3)).

\[
\ln k = \frac{E_a}{RT} + \ln A
\]  

The plot of \(\ln k\) versus \(1/T\) is always a straight line, as shown in Fig. 7. So \(E_a\) and \(A\) can be obtained.

The experimental data for the methanol elimination reaction over 2# and 3# are shown in Table 1. We obtained the activation energy \(E_{a2}\) 15.627 kJ/mol, \(E_{a3}\) 15.631 kJ/mol, the pre-exponential factor \(A_{2}\) 0.9899 s⁻¹, \(A_{3}\) 0.5176 s⁻¹. The experimental results agreed well with our assumption, therefore, the elimination of methanol accords to the first order dynamics. The photocatalytic activity of catalysts is 2# > 3#, which accords with the experimental results.

Table 1 Dynamic parameters over 2# and 3#

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3 Conclusions

For ZrO2/TiO2, CeO2/TiO2, H3PW12O40-ZrO2/TiO2 and H3PW12O40-CeO2/TiO2 composite catalysts prepared by the sol-gel method, their optimum activation conditions are as follows: ZrO2/TiO2 and H3PW12O40-ZrO2/TiO2 activated at 500°C for 2.5 h; CeO2/TiO2 and H3PW12O40-CeO2/TiO2 activated at 450°C for 3 h. At the flow rate of 7 mL/min and over 0.1 g catalyst, when the initial concentration of methanol is 4.8 g/m³, methanol can be eliminated completely by using CeO2/TiO2 or H3PW12O40-ZrO2/TiO2; when the initial concentration of methanol is 5.0 g/m³, the methanol can be eliminated completely over ZrO2/TiO2; when the initial concentration of methanol is 5.5 g/m³, the methanol can be eliminated completely over H3PW12O40-ZrO2/TiO2. The sequence of catalysts activity is as follows: H3PW12O40-ZrO2/TiO2 > ZrO2/TiO2 > CeO2/TiO2 ≈ H3PW12O40-CeO2/TiO2 > TiO2. After doping a certain amount of CeO2 and ZrO2, the particles of catalysts become smaller and more uniform, ZrO2 still enhances the thermal stability of TiO2, thereby improving their photocatalytic activity. The doping of H3PW12O40 enhances the activity; a certain synergy may have happened between the three components. The activation energy $E_{a28}$ and $E_{a38}$ are 15.627 and 15.631 kJ/mol, respectively. The pre-exponential factor $A_{28}$ and $A_{38}$ are as 0.9899 and 0.5176 s⁻¹. The curves of ln $k$ versus $1/T$ all exhibit linearity very well with a variance $R^2 > 0.99$, which accord to the first order dynamics law.

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References


