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Preparation of titania-based catalysts for formaldehyde photocatalytic oxidation from $TiCl_4$ by the sol–gel method

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Abstract

Titania sols were prepared by acid hydrolysis of a $TiCl_4$ precursor instead of titanium alkoxides. The effect of acid concentration on the particle size and stability of sol was investigated. Stable titania sols with mean particle size of 14 nm could be obtained when the H^+/Ti molar ratio was 0.5. The titania sols were modified with Pt, SiO_2, ZrO_2, WO_3 and MoO_3 to prepare a series of modified catalysts, which were used for the photocatalytic oxidation of formaldehyde at 37°C. They showed different photocatalytic activities due to the influence of the additives. Comparing with pure TiO_2, the addition of silica or zirconia increased the photocatalytic activity, while the addition of Pt and MoO_3 decreased the activity, and the addition of WO_3 had little effect on the activity. It is of great significance that the conversion of formaldehyde was increased up to 94% over the SiO_2–TiO_2 catalyst. The increased activity was partly due to higher surface area and porosity or smaller crystallite size. A comparison of our catalyst compositions with the literature in this field suggested that the difference in activity due to the addition of a second metal oxide maybe caused by the surface chemistry of the catalysts, particularly the acidity.

Keywords: Titania-based; Photocatalysis; Formaldehyde; $TiCl_4$; Sol–gel

1. Introduction

Photocatalytic oxidation of organic compounds in water and air has received much attention as a potential technology of pollution abatement. Several books and reviews have been published in this area [1–6]. The removal of volatile organic compounds (VOCs) in air has been a topic of major and continuing emphasis over the last decade [7–9]. Potential application sites for air purification and decontamination technologies include completely or partially enclosed atmospheres such as those found in spacecraft, office buildings, factories and homes. Titanium dioxide (TiO_2) has been extensively studied as a photocatalyst for the photocatalytic oxidation of organic compounds. A wide range of organic compounds can be oxidized to CO_2 and H_2O at room temperature on TiO_2 catalysts in the presence of UV or near-UV illumination [10–12]. However, slow reaction rates and poor solar efficiency (maximum 5%) have hindered the commercialization of this technology. In the hope of improving reaction rates, we dedicated much of our research in this area toward synthesis of better photocatalyst.

It has been shown that the photocatalytic activity of TiO_2 is influenced by the crystal structure, surface area, size distribution, porosity, band gap, and surface hydroxyl group density [13–16]. Recently, noble

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metals (Pt, Pd, Au, Ag, etc.) deposited on TiO_2 have been widely studied for the purpose of improving the latter's photocatalytic activity [17–21]. An enhancement of photocatalytic activity in the noble metal modified TiO_2 has been explained in term of a photoelectrochemical mechanism in which the electrons generated by UV irradiation on the TiO_2 semiconductor transfer to the loaded metal particles, while the holes remain in the semiconductor, resulting in a decrease in the electron-hole recombination [6]. In contrast to metal/TiO_2 photocatalysts, there have been few studies reported concerning the photocatalytic activity of metal oxide/TiO_2 catalysts. Fu and co-workers have reported that the mixtures of silica or zirconia with titania had significantly higher activities than pure titania for the complete photocatalytic oxidation of ethylene [24]. Do and Papp have found that degradation rates of 1,4-dichlorobenzene on WO_3/TiO_2 and MoO_3/TiO_2 systems were enhanced by the addition of ca. 3 mol% WO_3 and MoO_3 in titania [22,23]. However, Liu [25] has found that the photocatalytic activity of MoO_3/TiO_2 catalyst for the photooxidation of methanol was only one-fifth that of pure TiO_2.

It is well known that the sol–gel technology is an advanced method to prepare the mixed-metal oxide catalysts, which provides a highly controllable preparation route with inherent advantages such as molecular-scale mixing of the constituents, homogeneity of the sol–gel product and the use of different wet-chemical preparation tailoring tools [26]. In the traditional process, most of titania colloids are obtained by the controlled hydrolysis of titanium alkoxides. However, the synthesis of titania colloids from the corresponding salts (chloride, sulfate or nitrate) is lacking, which is possibly due to the rapid hydrolysis of the inorganic salt making the formation of precipitates become more easy and uncontrolled. In our early work, it was found that the fresh precipitate produced from the hydrolysis of either alkoxide or inorganic salt could be peptized with acid to yield a stable sol under appropriate conditions. The use of inorganic salt precursor rather than organic alkoxide precursor not only can reduce the cost of synthesis, but also can avoid the use of organic solvent to decrease pollution. In this paper, aqueous titania colloids were prepared from $TiCl_4$. A series of photocatalysts were obtained by modifying the titania colloids with Pt, SiO_2, ZrO_2, WO_3 and MoO_3. Formaldehyde was chosen as a probe for its presence and toxicity in air. The effects of the additives in titania on the structure, the photochemical properties and the photocatalytic activities were investigated by the physico-chemical methods such as X-ray diffraction (XRD), BET surface area, pore volume, UV–VIS diffuse reflectance spectroscopy (DRS) and photocatalytic oxidation of formaldehyde.

2. Experimental

2.1. Preparation of catalysts

All catalysts were prepared using the sol–gel method. The titania sols were prepared via acid peptizing the precipitate of $TiCl_4$ solution with ammonia. A 10% NH_4OH solution was dropped into the $TiCl_4$ solution and a white precipitate was obtained at pH = 7. The precipitate was washed with deionized water until the absence of Cl^- and NH_4^+ ions, then a certain amount of deionized water was added to form a suspension. By adding a correct amount 1.6 M HNO_3 ($[H^+]/[Ti] = 0.5$) with strong stirring for 24 h at 70°C, the precipitate was peptized to form a highly dispersed and stable titania sol. Appropriate amount of H_2PtCl_6, TEOS, $Zr(NO_3)_4$, $(NH_4)_2WO_4$ and $(NH_4)_2MoO_4$ solutions were dropped into the above titania sols, respectively. The modified sols were dried and calcined at 400°C to obtain Pt/TiO_2, SiO_2–TiO_2, ZrO_2–TiO_2, WO_3–TiO_2 and MoO_3–TiO_2 catalysts. The loading of Pt was 0.5 wt.%, and the contents of the other metal oxide in the modified catalysts were all 10 wt.%.

2.2. Reactivity measurements

The catalysts were packed into a 11 cm long and 2.4 mm diameter Pyrex tubular reactor. The weights of the catalysts were kept constant at 0.20 g and in all cases the illuminated length of the catalyst was identical. Illumination was provided by four 4 W UV bulbs, which produced a strong peak centered at 365 nm. Formaldehyde was mixed with a zero air stream to afford a reactant stream including 500 ppm formaldehyde. The reactant mixture flow rate was 20 ml/min. The temperature of the reactor under illumination was 37°C. Analysis of the reactor effluent was conducted with a HP6890 gas chromatograph.

2.3. Physicochemical analysis

The size of the sol particles was measured by quasi-elastic light scattering (QELS). Surface areas were calculated using nitrogen adsorption data at 77 K and BET analysis with OMNISORP 100CX Micromeritics. Porosities were determined from the adsorption maxima. X-ray diffraction analysis was performed using a Rigaku D/Max-RB X-ray diffractometer with a copper target at 40 KV and 100 mA. Crystallite sizes were calculated from the peak width by using the Schrerrer equation. UV–VIS diffuse reflectance spectra were recorded on a HITACHI 200-10 spectrophotometer. The sample for UV–VIS spectra was obtained by pressing the same-mass powder in a sample cell under the same pressure.

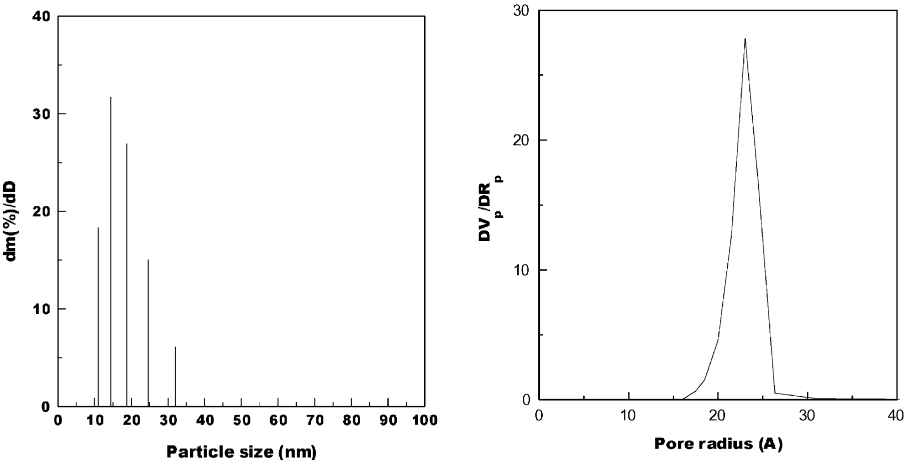
3. Results and discussion

3.1. Preparation of sols and catalysts

In the preparation process of titania sols, the acid concentration affected the size of the sol particles. Table 1 shows that the size of the sol particles, estimated from QELS measurements, varied with the acid concentration. It was found that the sol was the most stable and its mean particle size is the smallest when the H^+/Ti molar ratio was 0.5. Fig. 1a shows the size distribution of the titania sol prepared under the H^+/Ti molar ratio of 0.5. The size distribution of the particles was uniform and the most probably particle size was 14 nm. After calcination at 400°C, the pore size of the titania xerogel obtained was also very uniform and the mean pore diameter was about 4.6 nm (see Fig. 1b). For the modified catalysts, their pore sizes were also as uniform as that of pure TiO_2. Table 2 lists the surface area and pore structure parameters of the pure TiO_2 and the modified catalysts. For the Pt modified titania catalyst, the surface area, the pore

Table 1
The size of sol particles under different acid concentrations

No.	TiO_2 (mole/l)	H^+/Ti (mole ratio)	Particle size (nm)	Stability of sol
1	0.3125	0.08	–	Unpeptized
2	0.3125	0.2	102	Stable
3	0.3125	0.4	45	Stable
4	0.3125	0.5	14	Stable
5	0.3125	0.7	56	Stable
6	0.3125	1.0	96	Stable
7	0.3125	1.2	–	Unstable



(a) (b)

Fig. 1. (a) Particle size distribution of titania sols and (b) pore size distribution of TiO_2 xerogel prepared from this titania sol. The titania sol was obtained by acid hydrolysis of $TiCl_4$ when H^+/Ti molar ratio was 0.5. The size distribution of particles was measured by QELS at room temperature. TiO_2 xerogel was prepared by drying and calcining the above titania sol for 3 h at 400°C. The pore structure was studied by low temperature nitrogen adsorption with OMNISORP 100CX Micromeritics.

Table 2
Structural data for TiO_2-based catalysts

Sample	S_{BET} (m^2/g)	V_p (cm^3/g)	Porosity (%)	Crystallite size (nm)
TiO_2	72.1	0.131	33.8	8.5
Pt/TiO_2	80.4	0.140	35.3	9.4
SiO_2–TiO_2	229.8	0.156	37.8	6.2
ZrO_2–TiO_2	132.7	0.137	34.8	6.2
WO_3–TiO_2	129.6	0.128	33.3	7.8
MoO_3–TiO_2	139.7	0.095	27.0	6.7

volume and porosity were slightly higher than that of the pure TiO_2. For the binary metal oxide catalysts, the addition of a second metal oxide increased the specific surface area of the catalyst. Especially, the surface area of the SiO_2–TiO_2 catalyst was remarkably increased up to 229.8 cm^2/g. However, the effects of the additives on the pore volume and porosity were different. SiO_2–TiO_2 and ZrO_2–TiO_2 catalysts gave higher pore volume and porosity, while MoO_3–TiO_2 catalyst presented the lowest pore volume and porosity, which were 0.095 cm^3/g and 27%, respectively.

Fig. 2 shows the XRD spectra of these catalysts. All of the titania in these systems were in the anatase form, although a peak at d of 5.38 in WO_3–TiO_2 catalyst cannot be assigned. The crystallite size of these catalysts listed in Table 2 shows that modification by Pt increased the crystallite size, while the addition of a second metal oxide could decrease the crystallite size, especially for the addition of SiO_2 or ZrO_2.

3.2. Photochemical properties of catalysts

In most articles, UV–VIS band position is more often used to demonstrate the particle size or quantum effect. Fig. 3 shows the UV–VIS diffuse reflectance spectra of these catalysts. It was found that there was no obvious difference on their UV–VIS band position, which were close to the band position of the pure TiO_2. However, their UV–VIS absorption intensities were observably different. The intensity decreased with the order of SiO_2–TiO_2, ZrO_2–TiO_2, TiO_2, WO_3–TiO_2, Pt/TiO_2 and MoO_3–TiO_2. In the preparation process of binary mixed oxides, as calcination temperature increase, pairs of hydroxyl surface will combine to lose a water molecule and form a metal–oxygen–metal link to establish dissimilar oxide interface. An interaction between the additives and TiO_2 possibly change the surface region of the pure TiO_2. So, the photoelectric behavior of modified titania systems become more

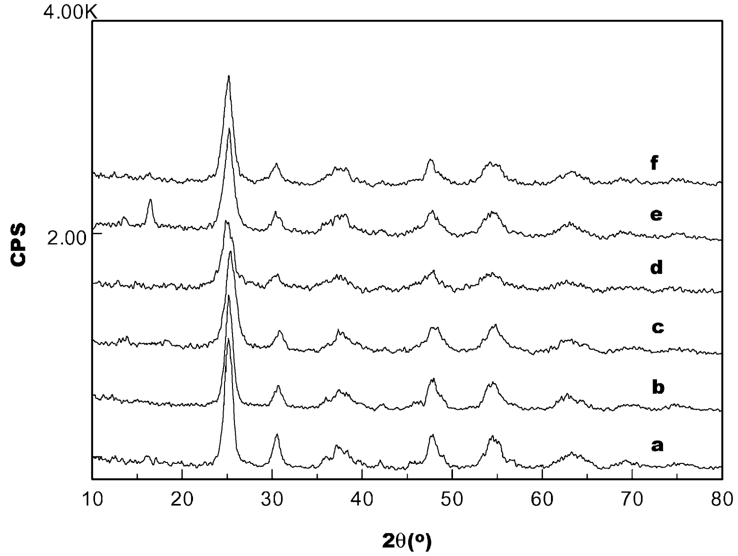


Fig. 2. XRD patterns of the catalysts (a) TiO_2; (b) Pt/TiO_2; (c) SiO_2–TiO_2; (d) ZrO_2–TiO_2; (e) WO_3–TiO_2; (f) MoO_3–TiO_2. The samples were calcined for 3 h at 400°C. X-ray diffraction analysis was performed using a Rigaku D/Max-RB X-ray diffractometer with a copper target at 40 KV and 100 mA.

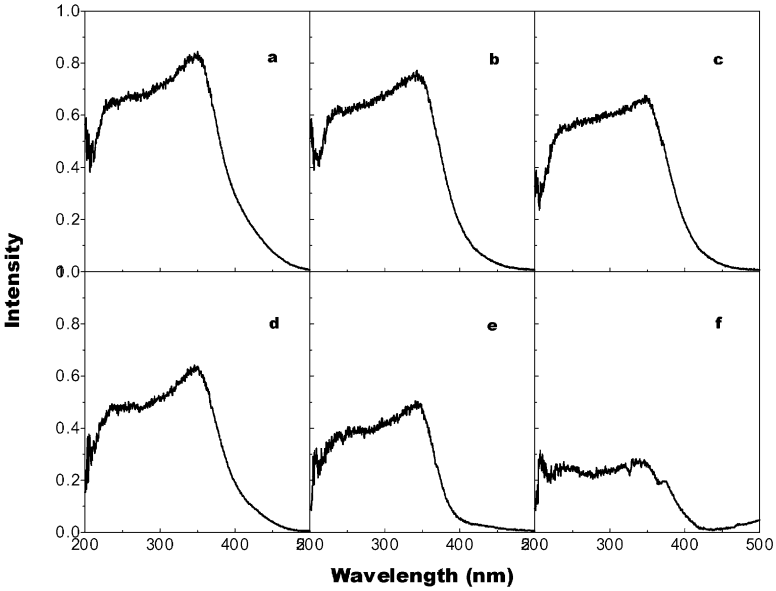


Fig. 3. UV–VIS diffuse reflectance spectra of the catalysts. (a) SiO_2–TiO_2; (b) ZrO_2–TiO_2; (c) TiO_2; (d) WO_3–TiO_2; (e) Pt/TiO_2; (f) MoO_3–TiO_2. The samples were calcined for 3 h at 400°C. UV–VIS absorption spectra were recorded on a HITACHI 200-10 spectrophotometer.

complicated. Due to the difference of additives in ionicity, coordination structure, electron or hole energy levels, etc., the properties of the interface between titania and additives are very different. Under UV-light illumination, it seems possible to result in current carrier with different concentrations on the materials modified by different additives, which has a great effect on the UV–VIS absorption intensities.

3.3. Photocatalytic activity of the catalysts

Conversions of formaldehyde over these modified catalysts and pure TiO_2 prepared from the titania sols are shown in Fig. 4. The conversion of formaldehyde over pure TiO_2 was 41%, while the modification of Pt in TiO_2 did not increase the photocatalytic activity as reported in most of the literature, and the conversion of formaldehyde was only 30%. By comparison, it was found that the effects of the addition of a second metal oxide on the photocatalytic activity were obviously different with the composition. Modification by silica or zirconia was shown to have significantly higher activities than pure titania. Moreover, the conversion of formaldehyde over the SiO_2–TiO_2 catalyst

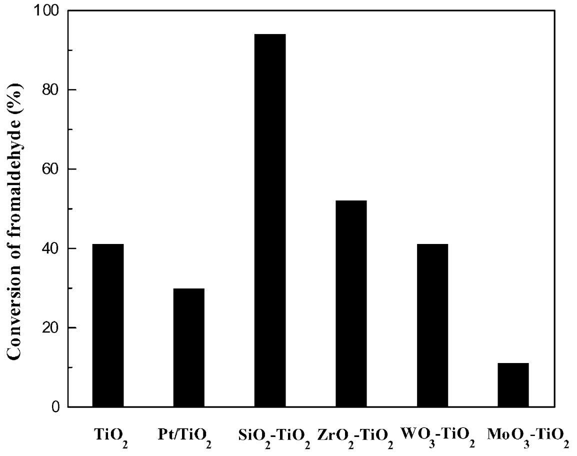


Fig. 4. Conversions of formaldehyde over different photocatalysts. The reaction was carried out on a home-made equipment. The weights of the catalysts were kept constant at 0.20 g. Illumination was provided by four 4 W UV bulbs. These bulbs produced a strong peak centered at 365 nm. Formaldehyde was mixed with a zero air stream to afford a reactant stream including 500 ppm formaldehyde. The reactant mixture flow rate was 20 ml/min. The temperature was kept at 37°C. Analysis of the reactor effluent was conducted with a HP6890 gas chromatograph.

Table 3
The total activity and specific activity of these catalysts

Catalyst	TiO_2	Pt/TiO_2	SiO_2–TiO_2	ZrO_2–TiO_2	WO_3–TiO_2	MoO_3–TiO_2
Total activity (%)	41	30	94	52	41	11
Specific activity ($\times 10^3$ μmol/s/m^2)	4.74	3.11	3.41	3.26	2.64	0.66

increased up to 94%, and such a high conversion of formaldehyde at low temperature is very important for the photocatalysis since all inhabited atmospheres of concern to humans exist at or near 20–30°C. It was found that the addition of WO_3 had little effect on the activity, while the addition of MoO_3 seriously decreased the conversion of formaldehyde that was only 11%.

As is shown above, the addition of the second metal oxide increased the surface areas and porosities of the catalysts, and decreased the crystallite size. The higher surface area and porosity and the smaller particle size of the SiO_2–TiO_2 probably caused the increase of the activity. The conversion of formaldehyde in Fig. 4 is values of total conversion of these catalysts. In order to declare the influence of surface area on the conversion of formaldehyde, values of total conversion of formaldehyde are divided by the catalyst surface area and expressed in terms of specific activity with units of μmol/m^2 (see Table 3). The results showed that the specific activities of the modified catalysts were lower than that of the pure TiO_2, which suggested that the surface area had important influence on the activity of the photocatalyst. In current statement, the reactive rate on per active site of the catalyst cannot be obtained because the active site population on the surface of catalyst is unknown. On the other hand, the specific activity of the catalysts cannot really reflect the reactive rate on per active site because the active site population and surface properties of the modified photocatalysts are very different with those of the pure TiO_2. However, it was found that the specific activity of SiO_2–TiO_2 catalyst is highest among these modified photocatalysts. Their specific activity decreased with the order of SiO_2–TiO_2, ZrO_2–TiO_2, Pt/TiO_2, WO_3–TiO_2 and MoO_3–TiO_2, which suggested that the chemical change on the catalyst surface would be possibly an important factor for the activity of photocatalyst.

It is interesting to note that there is a corresponding relation between the absorption intensity and the activity of the catalysts. The stronger the UV-absorption intensity, the higher the activity. It is well known that the semiconductors can act as a photocatalysts for light-induced redox process due to their electronic structure, which is characterized by a filled valence band and an empty conduction band. When a photon with an energy of $h\nu$ matches or exceeds the bandgap energy, E_g, of the semiconductor, an electron is promoted from the valence band into the conduction band, leaving a hole. The separate electron or hole would react with electron donors and electron acceptors adsorbed on the semiconductor surface to run the light-induced redox process. The strong absorption intensity implied that more electrons could be promoted from the valence band into the conduction band and more separate electrons or holes could be produced, which were help to enhance the photocatalytic activity.

In particular, It has been found that mixed oxides can develop very strong acidity even when the pure oxide components do not show it. Recently, increasing interest has been devoted silica-titania mixed oxides. Materials belonging to this system have been found to be even more acidic that silica-aluminas [27,28]. In this case, surface acidity is thought to take the form of stronger surface hydroxyl groups. These groups accept holes generated by illumination and, in turn, oxidize adsorbed molecules. Hole traps such as the hydroxyl groups prevent electron-hole recombination and, therefore, increase quantum yield. Thus, a greater number of surface hydroxyl groups may be expected to yield a higher reaction rate. In fact, zirconia and silica modified titania displayed some of the highest acidities among the binary metal oxides [27]. Silica is tetrahedrally coordinated with each oxygen bonding to two silicon atoms, and titania is octahedrally coordinated with each oxygen bonded to three titanium atoms. So, if a titanium atom enters a silica lattice, then each of its six bonds will be attached to an oxygen atom having only one other cation bond. Four valence electrons (on Ti) divided by six gives a charge imbalance of −1/3 per bond. Since the imbalance is negative, protons are expected to associate with the nearby oxygen atoms. There are now more surface hydroxyl groups than would be initially expected. Some experiments indicated that the titanium migrates into silicon sites in titanium-rich binary mixed oxides [29,30]. It has been found that the new acidic sites created by lattice substitution have Brönsted acid instead of Lewis acid characteristics [28,31]. It is well known that zirconia is eight-fold coordinated with each oxygen bonding to four zirconium atoms. If titania migrates into zirconia, the zirconia-modified titania displays Lewis acid. Modification by silica provides more surface hydroxyl groups that may be beneficial for the photocatalytic oxidation of formaldehyde. It is hoped that FTIR, XPS and NXANE studies in our lab will provide more insight and populations of surface groups in these mixed oxide photocatalysts. Further surface chemistry studies appear to be necessary to identify the rate enhancement mechanism with certainty.

4. Conclusion

Stable titania sols can be obtained by acid hydrolysis of $TiCl_4$ instead of titanium alkoxide when the H^+/Ti molar ratio is 0.5. The modification of the titania sol with different compositions can enhance or reduce the photocatalytic activity for the oxidation of formaldehyde. The modification of the titania sol by silica has been shown to produce a better photocatalyst for the oxidation of formaldehyde. Conversion of formaldehyde at 37°C can be increased up to 94% over SiO_2–TiO_2 catalyst. This substantial increase in activity is in part due to higher surface area and porosity or smaller crystallite size. The increase of UV absorption intensity also plays a significant role. In addition, the surface chemistry of catalysts, particularly the acidity, is also closely related to the photocatalytic activity.

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