Physico-chemical Properties of Nb/Ti Binary Oxides and their Photo-catalytic Activities

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A series of binary Nb/Ti oxides was prepared by co-precipitation. Their structure and physico-chemical properties in term of surface area, surface acidity, bandgap energy and life time of the radiation-excited electron-hole pair were examined. These properties were correlated to their catalytic activities in photo-degradation of oxygenated organic pollutants in water. The organic pollutants under investigation were phenol, cyclohexanol and tetrahydrofuran (THF). The lab-made titanium oxide and those doped with a small amount of Nb (molar ratio of Nb/(Nb+Ti) less than 20%) showed higher activities in degradation of the organic pollutants. However, the mineralization efficiencies were different for the three oxygenated organic pollutants. Nearly complete mineralization to form CO_2 could be achieved in the degradation of phenol. For cyclohexanol, only ca. 50% selectivity of CO_2 was obtained over all the catalysts. Similar low efficiency in complete mineralization was observed in the degradation of THF, but higher selectivity (ca. 65-75%) of CO_2 could be obtained on the binary oxide with Nb content less than 4 molar %. In contrast, the binary Nb/Ti oxide with equal Nb and Ti molar content gave the poorest catalytic activity. The photocatalytic activity is generally correlated well to the life time of the radiation-excited electron-hole pairs. The contribution of surface acidity to the photocatalytic activity was only demonstrated on the niobia-dominant oxide catalysts toward THF. The photocatalytic activity was found to have no correlation with the crystalline structure, the bandgap energy, the surface area or the surface hydroxyl density.

INTRODUCTION

Research in the photo-degradation of the harmful organic pollutants in waste water by semiconductor materials has been growing steadily over the last decade.[1] Titanium oxide is an n-type semiconductor and a typical photocatalyst. The advantage of utilization of titanium oxide in decomposition of organic pollutants includes its low cost, radiation stability, and no need of using strong oxidizing agents, such as O_3 or H_2O_2.[2]

Many factors were considered to influence the photocatalytic activity of TiO_2, such as the crystalline structure, particle size, bandgap energy, acidity and density of hydroxyl groups on the catalyst surfaces. However, the effect of these factors is still controversial. For instance, anatase is commonly found more active than rutile in photocatalysis.[3-5] Nevertheless, several studies showed that the activity was more influenced by the preparation method of the catalyst.[6-7] Surface acidity is another important factor commonly discussed. Studies on the acidity of either anatase or rutile by pyridine adsorption have demonstrated that the surface acidity is mainly of the Lewis type.[8-11] The commercial Degussa P-25 TiO_2, which has been the most frequently studied photocatalyst, contains 70% anatase and 30% rutile. The catalytic activity of Degussa P-25 TiO_2 in the photodegradation of 1,4-dichlorobenzene was reported to improve by impregnating a suitable amount of MoO_3, WO_3,[12] or Nb_2O_5.[13] In these cases, surface acidity was proposed to be the important factor affecting the efficiency of the catalysts. Binary oxides prepared by mixing other metal ions into TiO_2 through the co-precipitation method are more commonly studied. The effect of the second metal species on photocatalytic activities of the binary oxides however is quite varied. More enhanced photocatalytic activities in degradation of organic pollutants than on pure TiO_2 were reported on TiO_2 doped with a small amount of transition metal or lanthanide ions,[14-16] but lower activities were observed on Cr(III) and Ce(IV) doped TiO_2.[17,18] Mixed metal oxides often generate additional acid sites, especially Bronsted acid type. In several of these studies, the surface acidity was thought to contribute surface hydroxyl groups, which play an important role in stabilizing holes generated by illumination and oxidizing adsorbed molecules.[6,7] On the other hand, improved photocatalytic activities in decomposition of organic species were reported on TiO_2/SiO_2

Dedicated to Professor Sheng-lieh Liu on the occasion of his ninetieth birthday.

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and TiO_2/Al_2O_3[19,20] and TiO_2/molecular sieves.[21] The second metal oxide was considered to facilitate the adsorption of the organic substrates and make them more easily approach the active TiO_2 sites.

Niobium oxide and niobium compounds are interesting for their activities in catalysis. Hydrated niobium oxide was reported to have strong acidity and exhibit high activity in acid-catalyzed reactions.[22] Niobia, when used as a support, was reported to promote reactivity of platinum catalysts.[23,24] The effects were associated with the strong metal-support interaction, which was the phenomenon first observed on noble metals supported on TiO_2.[25] Besides, layered niobates demonstrated high activities in photo-decomposition of water and alcohols.[26-28] However, the photocatalytic activity of niobium oxide in degradation of organic pollutants has received little attention. In this study, a series of binary Nb/Ti oxides was prepared. Their activities in the photo-degradation of oxygenated organic compounds were compared in order to understand the factors which affect the photocatalytic activity.

EXPERIMENTAL METHODS

Catalyst Preparation

Reagent grade chemicals were used as purchased without further purification. $NbOCl_3$ solution was prepared by dissolving $NbCl_5$ (Janssen) in concentrated HCl (Janssen), followed by dilution to make 0.1 M solution. $TiOCl_2$ solution was prepared by mixing an equal weight of $TiCl_4$ (Merck) and 1.0 M HCl solution. The binary oxides of different Nb/Ti molar ratios were prepared by refluxing the stoichiometric mixture of $TiOCl_2$ and $NbOCl_3$ solutions for 3 h. The resultant solids were filtered, washed with doubly deionized water until free of Cl^- ions, and followed by drying at ambient temperature. The catalysts were named as NTs, where "s" represents Nb/(Nb+Ti) molar ratio in percentage.

Characterization Techniques

BET surface area was determined by physical adsorption of N_2 at liquid N_2 temperature in a volumetric system. The powder XRD patterns were examined with a Scintag X1 diffractometer using Cu K α radiation. The FT-Raman spectra were recorded using a BOMEM MB155 IR/Raman spectrometer with a Nd-YAG laser (1064 nm) source. Diffuse reflectance UV-Vis spectra of powder samples were obtained with a Shimadzu UV-2101PC spectrometer. The bandgap energies of the catalysts were determined based on the absorption threshold of their UV-Vis spectra. The lifetime of radiation-excited electron-hole pairs was monitored by examining the luminescence lifetime of the solid catalysts with a time-resolved spectrometer, in which 355 nm light source generated from a Nd-YAG laser was used and detection was set at 450 nm. The surface hydroxyl groups of powder samples were examined using a BOMEM MB155 IR spectrometer equipped with a Harrick diffuse reflectance cell. The acidity of the catalysts was determined by temperature programmed-desorption (TPD) of NH_3 using a Du Pont 951 TGA system.

Photocatalytic Activities

A Rayoney photochemical chamber reactor of model no. PRP-100 was used for photocatalysis study. Detailed setup of the apparatus was described previously.[7] The catalyst in powder form based on the same metal equivalence as 0.01 g TiO_2 (amount listed in Table 1), was suspended in a 50

Table 1. Phase Composition, Surface Area and the Weight Used in Photocatalysis of Nb/Ti Binary Oxides

Catalyst	Nb/(Nb+Ti) (%)	S. A. (m^2g^{-1})	Phase composition[a] (%)		Catal. wt[b] (g)
			Anatase	Rutile	
LR	0	141	0	100	0.0100
NT01	1	81	9	91	0.0100
NT04	4	105	20	80	0.0103
NT07	7	190	58	42	0.0105
NT11	11	190	64	36	0.0110
NT19	19	149	77	23	0.0113
NT50	50	228	88	12	0.0133
NT95	95	301	-[c]	-	0.0163
NT100	100	300	-	-	0.0166

[a] Determined by XRD patterns.
[b] The same metal equivalence as 0.01 g TiO_2.
[c] Amorphous phase.

mL aque ous so lu tion of 1.25 mM ox y gen ated or ganic compound. The or ganic sub strates un der in ves ti ga tion in cluded phenol, cyclohexanol and tetrahydrofuran. O_2 gas of 10 mL/min was bub bled through as ox i dant, and 300 nm UV ra-di a tion was the light source. The out let gases were di rected through a two-stage bub bling trap con tain ing sat u rated $Ba(OH)_2$ so lu tion, and the CO_2 yield was de ter mined based on the weight of $BaCO_3$ pre cip i tated. Gas prod ucts were an a lyzed off-line dur ing the re ac tion course. The liq uid prod ucts retained in aque ous so lu tion af ter 6 h ra di a tion were sep a rated with a Hewlett Packard 5890 GC us ing a Rtx-5 cap il lary column of 60 m length and de tected by a FID de tec tor.

RESULTS

Structure characterization

The crys tal line struc ture of the Nb/Ti bi nary ox ides was iden ti fied by x-ray dif frac tion (Fig. 1). Rutile was the crys tal-line phase ob served on pure ti ta nium ox ide, and the sam ple was termed LR (an ab bre vi a tion for lab-made rutile). As Nb of as low as 1% was doped into the ox ide, some ana tase phase ap peared. Based on the area ra tio of the peak at $2\theta = 25.3°$ for ana tase to that at 27.4° for rutile, the com po si tion of the crys-tal line phases in the bi nary ox ides was de ter mined and the results are tab u lated in Ta ble 1. The amount of the ana tase phase in creased with the Nb con tent. When ni o bium ox ide be came dom i nant, such as Nb/(Nb+Ti) mo lar ra tio ≧ 95%, the sol ids turned to amor phous.

The Raman spec tra of the sam ples with low Nb con tent showed two peaks at 603 and 437 cm^{-1} (Fig. 2), which are the char ac ter is tic Ti-O vi bra tional peaks of rutile.[29] These two peaks shift to ward 616 and 434 cm^{-1}, re spec tively, as Nb was added into the ox ide. When the Nb con tent is in creased to Nb/(Nb+Ti) ≧ 11%, two ad di tional peaks ap pear at 514 and 280 cm^{-1}. The 280 cm^{-1} peak grows with the in crease of Nb con tent, while the 514 cm^{-1} peak dis ap pears. For the bi nary ox ides of amor phous struc ture (NT95 and NT100), two very broad peaks ap pear at 636 and 280 cm^{-1}, which cor re spond to the vi bra tional modes of NbO_6 octahedra and Nb-O-Nb link-age, re spec tively.[30] The three char ac ter is tic vi bra tional peaks of ana tase TiO_2, which should ap pear at 640, 515 and 395 cm^{-1},[29] were not ob served in the Raman spec tra of the bi nary ox ides. These re sults in fer that the ana tase struc ture ob served in XRD pat terns is not due to pure TiO_2 struc ture. In stead, it

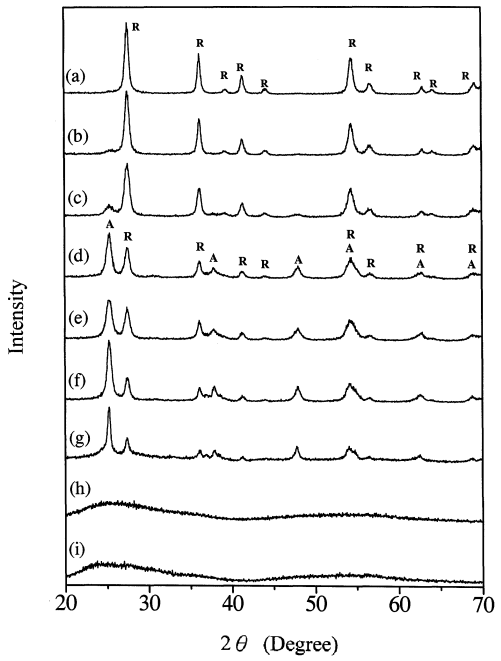

Fig. 1. XRD pat terns of as-prepared Nb/Ti bi nary ox-ides, (a) LR, (b) NT01, (c) NT04, (d)NT07, (e) NT11, (f) NT19, (g) NT50, (h) NT95 and (i) NT100; where A: ana tase and R: rutile.

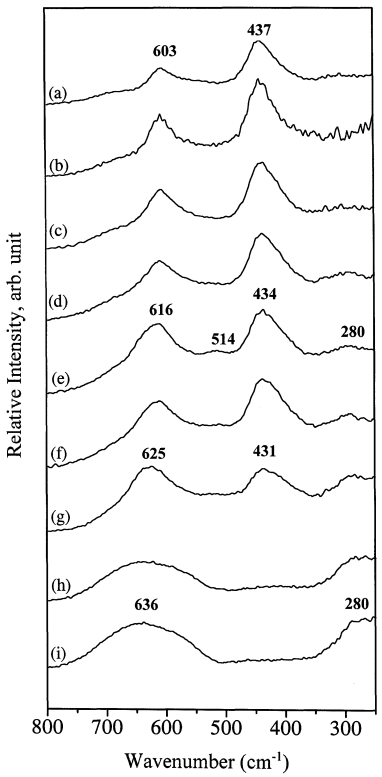

Fig. 2. Raman spec tra of as-prepared Nb/Ti bi nary ox-ides, (a) LR, (b) NT01, (c) NT04, (d)NT07, (e) NT11, (f) NT19, (g) NT50, (h) NT95 and (i) NT100.

should be an oxide of Nb and Ti mixed in the molecular level. Rutile is the densest phase of TiO_2 and thermodynamically most stable in comparison to other phases. The formation of anatase phase instead of rutile in Nb/Ti binary oxides is attributed to the perturbation of crystal growth when Nb(V) ions of relatively larger size and with excess positive charge than Ti(IV) were incorporated into the oxide structure. A similar phenomenon was also observed on the growth process of nanosize rutile, where the crystalline phase was greatly influenced by the addition of NH_4Cl as mineralizer.[31]

Fig. 3 shows that all samples have adsorption in the O-H stretching vibration region. The as-prepared samples show broad absorption bands covering 2500-3750 cm^{-1} region, demonstrating the presence of H-bonding among the O-H groups and the physical-adsorbed water molecules. The intensity of the broad bands was markedly reduced and discrete peaks appeared after the samples were evacuated at 400 °C. Lab-made TiO_2 has the peak maximum appearing at 3670 cm^{-1}, lab-made Nb_2O_5 at 3686 cm^{-1}, and the binary oxides show a combination of both peaks in different intensity ratios.

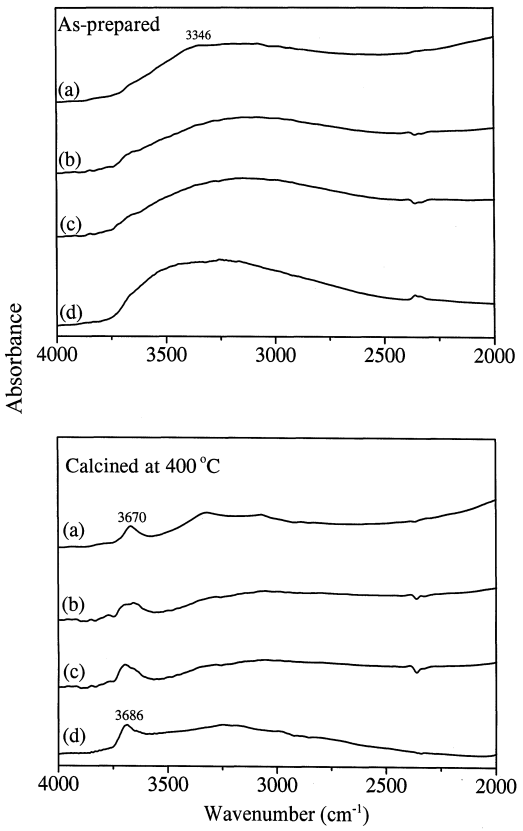

Fig. 3. Diffuse reflectance IR spectra in the O-H stretching region of as-prepared and calcined Nb/Ti binary oxides, (a) LR, (b) NT11, (c) NT50 and (d) NT100.

Other physico-chemical properties

The physico-chemical properties of Nb/Ti binary oxides of various Nb contents in term of surface area, surface acidity, bandgap energy and lifetime of the radiation-excited electron-hole pair are summarized in Fig. 4. The binary oxides except those with amorphous structure have similar bandgap energies as that of lab-made rutile TiO_2 (LR), while the niobia dominant samples NT95 and NT100 show an apparent blue shift relative to either lab-made rutile (3.04 eV) or commercial Nb_2O_5 (2.86 eV). These two amorphous oxides concomitantly have the highest BET surface area and surface acidity. Since the higher the surface area, the smaller the particle sizes, the blue shift of the bandgap energies is likely a result of the particle size quantization effect.[32] Fig. 4 also shows that the acid amounts are similar for the binary oxides of Nb contents smaller than 50%, while the BET surface area generally increases with Nb content. Both values however reach the maximum for niobia-dominant samples. On the other hand, the luminescence lifetime has little correlation

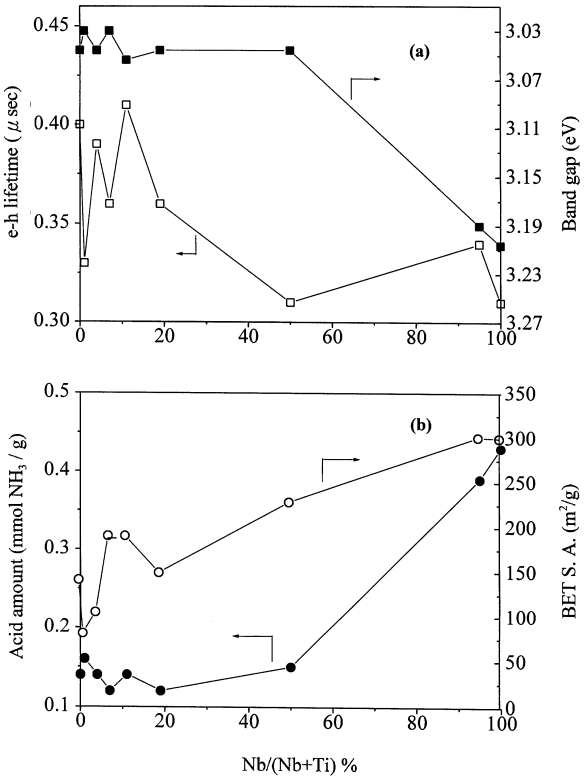

Fig. 4. Physico-chemical properties of Nb/Ti binary oxides as a function of Nb content, (a) luminescence lifetime and bandgap (b) acid amount and BET surface area.

with the Nb content. The inversion of the life time is proportional to the electron-hole recombination rate. The results oppose the proposal that larger bandgap energy generally has lower recombination rate.[33] The longest life times were observed on lab-made rutile TiO_2, as well as the binary oxides containing 4 and 11% Nb, while the shortest life times were found on pure Nb_2O_5 and NT50.

Photocatalytic activities of TiO_2 of different crystalline phases

The results of photo-decomposition of oxygenated organic substrates in aqueous solutions over lab-made-rutile (LR) were compared with those over commercial TiO_2 and tabulated in Table 2. Although the commercial anatase TiO_2 shows the highest conversions based on the disappearance of the organic substrates, its efficiencies in complete mineralization to form CO_2 are rather low. The mineralization efficiency was also found to vary with the organic substrate. It decreases from 55.4, 34.1 to 14.2% for phenol, THF and cyclohexanol, respectively. On the other hand, the commercial rutile TiO_2 shows very low activities in degradation, which is consistent with most of the literature results. On the contrary, lab-made rutile gave relatively high conversions and mineralization efficiencies. Moreover, it is much more efficient than the commercial anatase in complete oxidation of the organic substrates to CO_2. These results demonstrate that the crystalline phase is not a key factor in determining the catalytic activity of photodegradation.

In order to examine the effect of catalyst surface area, photo-degradation of phenol was carried out with lab-made rutile calcined at different temperatures but based on a catalyst amount of the same total surface area. Table 3 shows that both the conversion and the mineralization efficiency decrease with the calcination temperature of rutile. The results rule out that the catalytic activity is proportional to the surface area. Instead, the number of surface hydroxyl groups is probably more important.

Photocatalytic activities of the Nb/Ti binary oxides

Fig. 5 shows the photo-degradation rates of the three organic substrates over the Nb/Ti binary oxides of various Nb contents. The highest conversion and mineralization efficiency were observed over the binary oxides with Nb content lower than 11%, while the minimum activities were observed over the binary oxides with Nb/Ti molar ratio higher than 1. The maximum activity however varied with different organic substrates. Based on the disappearance of organic reactant, the highest activities for the three substrates are: lab-made rutile for phenol, NT07 for cyclohexanol, and NT01 for THF. On the other hand, the highest mineralization efficiencies are: NT11 for phenol, lab-made rutile for cyclohexanol, and NT01 for THF.

Table 2. Photodegradation of the Oxygenated Organic Substrates over Various TiO_2 Catalysts

Catalyst	Organic substrate	Conv. (%)	CO_2 Yield (%)	Miner. Eff.[a] (%)
Anatase	Phenol	100	55.4	55.4
(Commer.)	Cyclohexanol	98.6	14.0	14.2
	THF	70.0	23.9	34.1
Rutile	Phenol	56.5	20.5	36.3
(Commer.)	Cyclohexanol	40.0	2.4	6.0
	THF	37.3	13.1	35.1
LR	Phenol	87.9	75.4	85.8
(Lab-made	Cyclohexanol	72.7	38.4	52.8
rutile)	THF	73.4	55.0	74.9

[a] Miner. Eff. = mineralization efficiency.

Table 3. Photodegradation of 1.25 mM Phenol over Lab-made Rutile TiO_2 Based on the Same Surface Area

Calc. Temp. (°C)	S.A. (m^2/g)	Catal. Wt. (g)	Conv. (%)	CO_2 Yield (%)	Miner. Eff. (%)
25	141	0.0100	87.9	75.4	85.8
400	74	0.0191	83.6	63.0	75.4
700	23	0.0613	63.3	42.2	66.7

DISCUSSION

Effect of the organic substrates

The interaction of the organic substrates with the surface generated·OH radicals was considered to be the primary step of the photo-degradation in aqueous solutions.[2,34] Phenol is the most electrophilic among the three organic substrates. Over TiO_2 catalysts of different crystalline phases, the conversions of phenol in photo-degradation are always higher than those of THF and cyclohexanol. However, that changed on the binary oxides. For the binary oxides of low Nb content, phenol is no longer the one achieving the highest conversion. Over several catalysts, the conversions of cyclohexanol are over that of phenol. The dielectric constants of these three compounds decrease in the order of cyclohexanol (ε = 16.4) > phenol (ε = 12.4) > THF (ε = 7.5). Since there are hydroxyl groups on the catalyst surface, the high affinity of cyclohexanol to the catalyst surface may account for the high conversion of cyclohexanol.

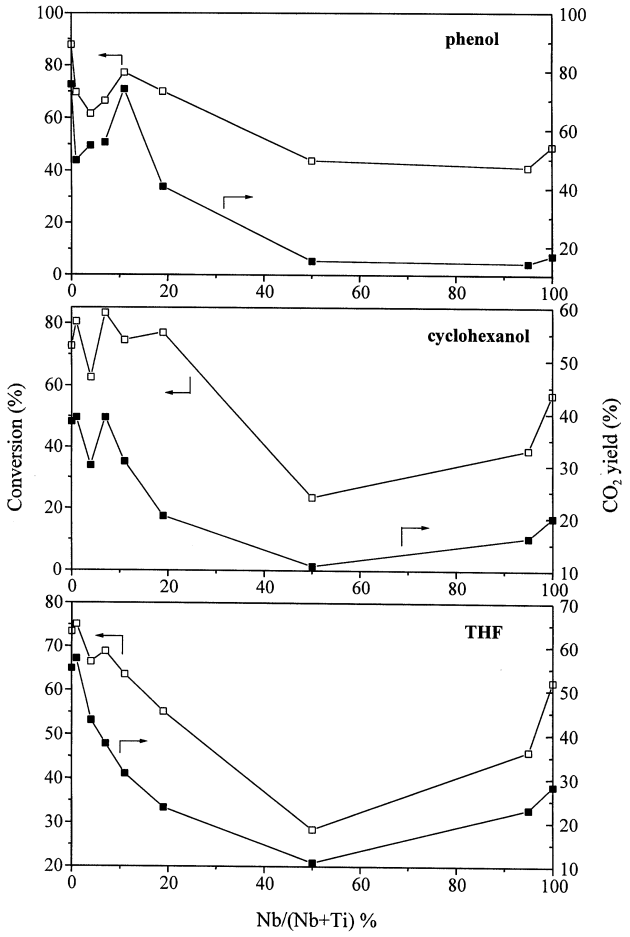

Fig. 5. Activities of photo-degradation of phenol, cyclohexanol, and THF over Nb/Ti binary oxides of various Nb contents: (○) conversion, (△) CO_2 yield, and (■) mineralization efficiency.

For niobia dominant oxides, THF has higher conversions than the other two organic substrates. Therefore, there must be factors other than electrophilicity and dielectric constant of the organic substrates which influence the photo-degradation activity. Besides, the mineralization efficiencies of phenol are very high over the binary oxides with Nb content less than 11%. The efficiency decreases as the Nb content increases. It is also noticed that over the binary oxides of low Nb contents the mineralization efficiencies of cyclohexanol are the lowest among the organic substrates. Therefore, cyclohexanol should generate stable intermediates which are volatile or difficult to decompose, such as cyclohexanone.

Factors on the catalysts affecting the photocatalytic activity

The Nb/Ti binary oxides of low Nb contents show higher photocatalytic activities than those of niobia dominance. The minimum activities were observed over catalyst NT50 containing equal equivalencies of Nb and Ti. Lab-made TiO_2, which has rutile structure, is among the oxides of highest activities, while NT50, which contains 88% anatase and 12% rutile phase, has lowest activity. The results are contrary to those observed on the commercial anatase and rutile TiO_2. It demonstrates that the crystalline phase of the semiconductor plays little role on photocatalytic activity. Instead, the preparation method is more important in obtaining the catalysts of high photoactivity.

Effect of surface hydroxyl groups

Sclafani et al.[6] attributed the high photoactivity of lab-made TiO_2 to surface hydroxyl groups, which were considered to trap the holes in the valence band and enhance the chemisorption of oxygen molecules in the conduction band. In the present system, FT-IR study shows no significant differences in the amount of surface hydroxyl groups among the Nb/Ti binary oxides of different Nb contents. Therefore, surface hydroxyl groups are probably not the key factor responsible for the differences in photocatalytic activities of the binary oxides.

Effect of bandgap, surface area and hot-electron life time

In comparison to the physico-chemical properties of the binary oxides shown in Fig. 4, the photocatalytic activities were found in rather good agreement with the hot-electron life time. Markedly, the minima on the activity profiles are consistent with those of luminescence life time. All

cor re spond to cat a lyst NT50, the bi nary ox ide with equal equiv a len cies of Nb and Ti. The photocatalytic ac tiv ity on the other hand has lit tle to do with the bandgap en ergy, since both bi nary ox ides of the high est and low est photocatalytic ac tiv i-ties have sim i lar bandgap en er gies. Be sides, the photo cata-lytic ac tiv ity does not in crease with the sur face area or the acid amount. How ever, that pure Nb_2O_5 is more ac tive in deg-ra da tion of all three or ganic sub strates than NT95 is con trary to the vari a tion of the lu mi nes cence life time. Hence, there must be fac tors other than the hot-electron life time that af fect the photocatalytic ac tiv ity. Since both niobia dom i nant sam-ples have sim i lar sur face ar eas but NT100 has greater sur face acid ity than NT95, sur face acid ity should con trib ute to some ex tent to the photocatalytic per for mance.

Ef fect of struc tural de fects

An other fac tor been brought to con sid er ation re cently is the struc tural de fects. Sclafani and Herrmann[35] re ported that the struc tural de fects on the sur face could photoadsorb ox y gen and form O^- and O^{2-} spe cies. In aque ous so lu tions, these spe cies are con sid ered to re act with sur face ad sorbed water molecules to gen er ate ·OH radicals. Based on the bandwidths at half-maximum of the x-ray dif frac tion peaks in Fig. 1, the NT50 sam ple, which gives the low est cat a lytic ac-tiv i ties, con com i tantly has the high est crystallinity among the bi nary ox ides. On the other hand, the bi nary ox ides of low Nb con tents have broad dif frac tion peaks, in di cat ing rel a-tively low crystallinity, while the niobia dom i nant ox ides have amorphous structure. Ac cord ing to the pro posal by Sclafani and Herrmann,[35] the struc tural de fects in crease the ox y gen-exchange abil ity of TiO_2. The ad sorbed ox y gen re-acts with the hot elec trons to form O^- and O^{2-} spe cies and that fur ther con verts to ·OH rad i cals. In the pres ent study, the struc tural de fects are con sid ered im por tant in in flu enc ing the lifetime of the hot elec trons and con se quently the photo-catalytic ac tivity.

Ef fect of acid ity

The im por tance of acid ity on photocatalytic ac tiv ity is dem on strated by the trend of the deg ra da tion rates of the three or ganic sub strates. The en hance ment of photoactivity by sur face acid ity was most ob vi ous over the niobia dom i nant sam ples NT95 and NT100, which have great est sur face acid-ity among the bi nary ox ides. In com par i son of the ac tiv ity pro files of the three or ganic sub strates shown in Fig. 5, the ex tent of en hance ment de creases in the or der of THF > cyclo-hexanol > phe nol. Sur face acid ity is re ported to im prove the photo-catalytic ac tiv ity by fa cil i tat ing the ad sorp tion of ba sic sub strates to the cat a lyst sur face.[20] The in ter ac tion should be weak for phe nol since it is it self an acidic com pound. Be-sides, acid is usu ally con sid ered a cat a lyst in break ing bonds of ethers. Hence, the en hance ment of the photo-degradation ac tiv ity by acid ity is most ob vi ous for THF and least for phe-nol.

More over, both niobia-dominant cat a lysts were found to give se ri ous cok ing dur ing the photodegradation re ac tions. Hence, the acid ity prob a bly also sta bi lizes coke prod ucts formed on the sur face. The cov er age of cat a lyst sur face with dark coke would re duce the quan tum yield and lower the min-er al iza tion ef fi ciency. As a re sult, the min er al iza tion ef fi cien-cies over the niobia-dominant ox ides are gen er ally lower than those over the ti ta nia-dominant ox ides.

CONCLUSIONS

We demonstrated that the crystalline structures of lab-made Nb/Ti bi nary ox ides vary with the ni o bium con tent, from rutile, a mix ture of rutile and ana tase, to amor phous com pounds. The bandgap en er gies of the bi nary ox ides re-main con stant for Nb con tent up to 50 mo lar %. Par ti cle size quantization ef fect was dem on strated on the vari a tion of the bandgap en ergy. The bandgap en er gies are low est but the sur-face ar eas and acid amount are great est for niobia-dominant ox ides. How ever, the photocatalytic ac tiv ity was found to have lit tle to do with the crys tal line struc ture, the bandgap, the sur face area and sur face hydroxyl den sity. The high est con ver sion and min er al iza tion ef fi ciency in photodegrada-tion of the three ox y gen ated or ganic sub strates were ob served over lab-made rutile and the bi nary ox ides with Nb/(Nb+Ti) mo lar ra tio less than 11%. The photocatalytic ac tiv i ties of the bi nary ox ides as a func tion of Nb con tent in deg ra da tion of the three ox y gen ated or ganic sub strates un der in ves ti ga tion var ied in sim i lar pat terns. The min ima were ob served over the bi nary ox ide with 1:1 Nb/Ti mo lar ra tio. The max i mum ac tiv i ties how ever vary with dif fer ent or ganic sub strates: lab- made rutile for phe nol, NT07 for cyclohexanol, and NT01 for THF. The struc tural de fects on the ox ides are con sid ered more im por tant than other fac tors in sta bi liz ing the life time of the hot elec trons and in creas ing the photocatalytic ac tiv i-ties. Be sides, sur face acid ity may also en hance the deg ra da-tion of the or ganic sub strates. For the three ox y gen ated or-ganic sub strates un der in ves ti ga tion, phe nol is most eas ily de graded over TiO_2 cat a lysts. As the in flu ence of acid ity in-creases over niobia-dominant ox ide, THF has higher con ver-sion than cyclohexanol and phe nol. How ever, a large num ber of acidic sites on the cat a lyst sur face also re duces the min er-al iza tion ef fi ciency due to se ri ous cok ing on the sur face.

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Key Words

Nb/Ti binary oxides; Catalytic; Photo-degradation; Organic pollutants.

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