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Characterization and photocatalytic activity of transition-metal-supported surface bond-conjugated TiO_2/SiO_2

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Abstract

$TM/TiO_2/SiO_2$ photocatalysts were prepared by the photodeposition method using transition metal salts (TM $= Fe^{3+}$, Co^{2+}, Ni^{2+} and Cu^{2+}) as precursors and the surface bond-conjugated TiO_2/SiO_2 as supporter in N_2 atmosphere, and were characterized by XRD, XPS, UV-Vis diffuse reflection and zeta-potential. Their photocatalytic activities were evaluated using reactive brilliant red K-2G (K-2G) and cationic blue X-GRL (CBX) showing different adsorption behavior on the oxides. Fe, Cu supported TiO_2/SiO_2 can efficiently extend the light absorption to the visible region. XPS analysis verified that the introduction of transition metal lead to the changes of the electronic environmental of Ti cations and the zeta-potential of oxides. As a result, K-2G has higher adsorption on the modified TiO_2/SiO_2 than that on the baked one, while the adsorption of CBX has a little change on the both oxides. At the same time, for the photodegradation of K-2G, Fe^{3+}, Co^{2+}, Ni^{2+}-modified catalysts show that their photoactivities are 3.3–2.2 times higher than the bare one. On the contrast, all transition-metal-supported catalysts have no significant activity improvement except that $Fe/TiO_2/SiO_2$ shows 1.68 times higher activity for the photodegradation of CBX. The results indicate that the photoactivity could be increased in photodegradation of dyes by changing the performances of adsorption to dyes and absorption to light of photocatalyst.

Keywords: Transition metal; Sensitization; TiO_2/SiO_2; Photodeposition; Dyes; Photocatalysis; Wastewater

1. Introduction

TiO_2 is the most widely used photocatalyst, due to its optical and electronic properties, low cost, chemical stability and non-toxicity. Due to its band-gap energy, TiO_2 utilizes only a very small fraction of the solar spectrum and thus doping with transition metals has been employed to extend the light absorption to the visible region [1–5]. The presence of foreign metal species is generally detrimental for the degradation of organic species in aqueous system, but many controversial results are reported. The modified photocatalyst is more active for one compound, but it is unavailable for another one. The effect of the additive metal species on the photoactivity depends on the support (previous catalyst), the preparation methods and degraded pollutant.

Some has dealt with the photocatalytic deposition of Pt and other metals on TiO_2 powders and suggested the application of this technique to the preparation of supported catalysts [6]. The photodeposition technique yields more active photocatalyst [7–9]. The photodeposition process involves the reduction of metal ions by cb electrons, the anodic process being the oxidation of water by vb holes. Oxidizable additives are generally added to improve the rate of deposition, as acetate, formaldehyde, methanol or 2-propanol.

In previous paper, we have shown that surface bond-conjugated TiO_2/SiO_2 photocatalyst has higher photoactivity than TiO_2 powder in eliminating azodyes. However, the catalyst could not be excited by visible light. In this present, metal-modification TiO_2/SiO_2 by photodeposition technique was investigated. Fe, Co and Ni have a suitable quantity of holes in the d-band. The addition of these metals can change photocatalytic performance of TiO_2/SiO_2. Therefore, Fe, Co, Ni and Cu were loaded on the surface of the catalyst under UV illumination with N_2 atmosphere and addition of acetic acid. These metal-supported catalysts were evalu-

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ated by the photodegradation of reactive brilliant red K-2G and cationic blue X-GRL, which have different adsorption behavior. The relationship between the photoactivity of the catalyst and reactant were discussed.

2. Experimental

2.1. Materials and method

Tetrabutyl titanate (Chemical Purity) was from Changcheng Chemical Company, Beijing. Silica gel was purchased from Qingdao Chemical Factory, China. Reactive brilliant red K-2G (K-2G) and cationic blue X-GRL (CBX) (Shanghai Chemical company) were used without further purification. All other chemical reagents are analytical purity.

Preparation of photocatalysts. Silica gel was dried and impregnated with cyclohexane solution of $Ti(OC_4H_9)_4$ for 15 h. After the cyclohexane solvent was completely vaporized at 313 K, the silica gel was dried at 393 K for 6 h, and calcined in the air in three different steps: 473 K for 1 h, 623 K for 1 h, and then 723 K for 8 h.

Metal-modified TiO_2/SiO_2 catalysts (M: Fe, Co, Ni and Cu). A variety of $TM/TiO_2/SiO_2$ photocatalysts were prepared by photodeposition in a way similar to the method used by Kraeutler and Bard [10]. Photodeposited 1% $Fe/TiO_2/SiO_2$, 1% $Co/TiO_2/SiO_2$, 1% $Ni/TiO_2/SiO_2$, 1% $Cu/TiO_2/SiO_2$ were synthesized in a deaerated system (N_2 atmosphere) by 300 W high-pressure mercury lamp (>330 nm)—illumination of 275 ml of suspensions containing 15 ml acetic acid, 5 g TiO_2/SiO_2 and the metal salt solution required for 15 h. The suspension was then centrifuged and the supernatant was removed for atomic absorption spectrometry (AAS) analysis (in all cases, the photoreduction of tested metal ions is nearly 100% to the completion). Then the catalysts became gray, and were washed with deionized H_2O to eliminate some ions produced from photodeposition process and became white, finally, the catalysts were dried at room temperature. All preparation experiments were carried out in a fluidized bed photoreactor, which consists of a 400 ml cylindrical glass body with sampling port, gas outlet port and gas inlet at the bottom of the glass body. A 300 W high-pressure mercury lamp surrounded glass thimble (>330 nm) was located in the center of the reactor. The reaction solution was suspended and deaerated by N_2 bubbling at 340 ml min^{-1}.

2.2. Characterization of $TM/TiO_2/SiO_2$

The $TM/TiO_2/SiO_2$ particles were analyzed by X-ray diffraction patterns using Cu Kα radiation ($\lambda = 1.54059$ Å) on a D/Max-RC X-ray diffractometer. Diffraction patterns were taken over the 2θ range of 20°–80°. To confirm the morphology of metal loaded on the catalyst, X-ray photoelectron spectra were recorded with a VG AM-08-09-2000 XPS instrument using the Al $K\alpha_{1.2}$ excitation source. Calibration of the spectra was done at the C 1s peak of surface contamination taken at 284.6 eV. The zeta-potential of the catalyst was measured for suspensions containing 0.1 g l^{-1} of titania/silica in 1 mM KNO_3 with Model JS94F micro-electrophoresis apparatus (Shanghai). The isoelectric point of the catalyst was obtained by the measurement of the zeta-potential. The UV-Vis diffuse reflectance spectra (DRS) of the samples in the wavelength range of 200–800 nm were determined using a spectrophotometer (Hatch UV 3010) with 150ϕ integral ball.

2.3. Photocatalytic activity measurements

The tested photoreactor is the same as that one used in preparation of $TM/TiO_2/SiO_2$. A 300 W high-pressure mercury lamp surrounded glass thimble (330–450 nm) was located in the center of the reactor. The photocatalytic activities of various catalysts were evaluated by measuring the decolorization of reactive brilliant red K-2G or cationic blue X-GRL. In typical experiments, 1.5 g catalyst was suspended in 275 ml of 20 mg l^{-1} reactive brilliant red K-2G or cationic blue X-GRL aqueous solution by air bubbling at 340 ml min^{-1}. Prior to irradiation, the suspension aqueous solution was mixed continuously in dark for 30 min to ensure adsorption/desorption equilibrium. The concentration of substrate in bulk solution at this point was used as the initial value for the further kinetic treatment of the photodegradation processes. Variations in the concentration of dyes in each degraded solution were monitored using 752 model UV-Vis spectroscopy (Shanghai). The $SO_4{}^{2-}$ ions were determined by ionic chromatography (Dionex Series 4500!).

3. Results and discussion

3.1. Catalyst characterization

3.1.1. XRD and XPS analysis

The XRD patterns showed that only anatase was found in all samples of transition-metal-supported TiO_2/SiO_2. No peak from transition metal was observed. The result indicated that the supported metals were uniformly dispersed and was not packed crystal. We have shown the structure of TiO_2/SiO_2 in detail in the previous paper [11]. In this paper, the transition-metal-supported TiO_2/SiO_2 will be discussed in detail. The samples of $Fe/TiO_2/SiO_2$, $Co/TiO_2/SiO_2$, $Ni/TiO_2/SiO_2$ and TiO_2/SiO_2 were investigated by X-ray photoelectron spectroscopy. The binding energy values of Fe 2p, O 1s, Si 2p and Ti 2p photoelectron peaks as determined by XPS of the above catalysts are summarized in Table 1. Fig. 1 shows the XPS spectra of $Fe/TiO_2/SiO_2$. Clearly, iron was loaded on the surface of TiO_2/SiO_2. The binding energy of Ti 2p (459.0 eV) of $Fe/TiO_2/SiO_2$ is higher than that of TiO_2/SiO_2 (458.4 eV). It revealed that the introduction of Fe changed the chemical environment

Table 1
XPS binding energies for the selected photocatalysts

Catalyst	BE (Ti 2p) (eV)	BE (Si 2p) (eV)	BE (O 1s) (eV)	BE (TM 2p) (eV)
TiO_2/SiO_2	458.4	103.3	532.5, 530.0	–
$Fe/TiO_2/SiO_2$	459.0	103.5	533.0, 530.5	Fe 2p: 711.6
$Co/TiO_2/SiO_2$	458.8	103.5	533.0, 530.3	–
$Ni/TiO_2/SiO_2$	458.8	103.5	532.8, 530.3	–

of the lattice Ti. The binding energy of Fe 2p is 711.6 eV which agrees with that of Fe 2p in Fe_2O_3 shown in table. The result indicated that Fe was supported on the surface of TiO_2/SiO_2 by Fe_2O_3 formation, resulting the changes of the XPS bands of O 1s core level (Fig. 2A). There are three types of O 1s in peaks in the TiO_2/SiO_2, corresponding respectively to oxygen in Si–O–Si, Ti–O–Ti and Si–O–Ti which has been reported [12]. There should be one type of O 1s to belong to Fe–O–Fe in $Fe/TiO_2/SiO_2$ based on above results. The electronic environment of the Ti cation is affected by the number of bonds with oxygen and also by the coordination number of these oxygen ligands. As a result, several types of titanium cation can exist at different metal addition. And different photoactivities of TiO_2 occur. The XPS photoelectron peaks of Co 2p and Ni 2p were not determined due to the lower amount in $Co/TiO_2/SiO_2$ and $Ni/TiO_2/SiO_2$. However, the binding energies of Ti 2p of the two catalysts were higher than that of TiO_2/SiO_2. It indicated that the chemical environment of the lattice titanium were changed. Their XPS bands of O 1s core level are shown in Figs. 2B and C. Obviously, all the peak position and shape took a great changes compared with the unmodified catalyst. The results implied that the both transition metal Co and Ni have been supported on the catalyst although they are not detected by XPS. The introduction of these transition metals changes different types of Ti cation, resulting in different photocatalytic performance.

3.1.2. UV-Vis DRS analysis

One can observe that $Fe/TiO_2/SiO_2$, $Cu/TiO_2/SiO_2$ differ from TiO_2/SiO_2 (shown in Figs. 3 and 4). Their absorption edges are in the vicinity of 500–600 nm, thus shifting the bandgap position to about 2.0 eV. Moreover, $Cu/TiO_2/SiO_2$ shows a new peak at 600–800 nm. This justifies why the both catalysts can be potentially good candidate for using the visible light. It should be noted that the enhanced absorption of the catalyst is necessary condition but not sufficient for its for improving photoactivity because the photo-efficiency depends on some factors concerned in photocatalytic degradation, which was observed in the activity studies below. The results also indicate that Cu and Fe have been loaded on the surface of TiO_2/SiO_2. No significant difference is observed among these UV-Vis DRS of $Co/TiO_2/SiO_2$, $Ni/TiO_2/SiO_2$ and TiO_2/SiO_2.

3.1.3. Catalyst zeta-potential

Fig. 5 shows that the zeta-potential of the catalysts changes with pH of solution increasing. The iso-electric points of $Fe/TiO_2/SiO_2$ and TiO_2/SiO_2 are about 3.0 pH units, while that of the other two catalysts modified by

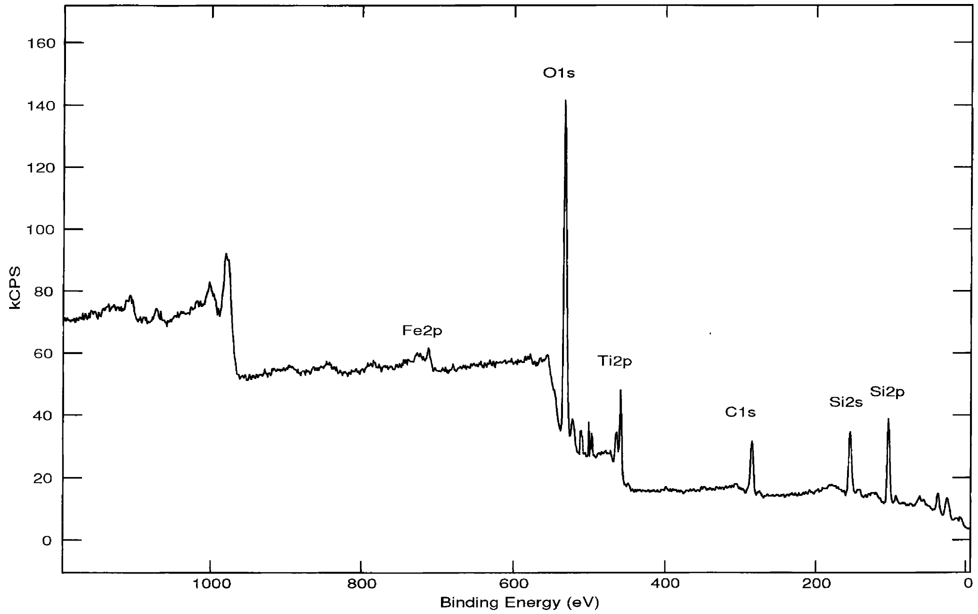

Fig. 1. XPS spectra for $Fe/TiO_2/SiO_2$ photocatalyst.

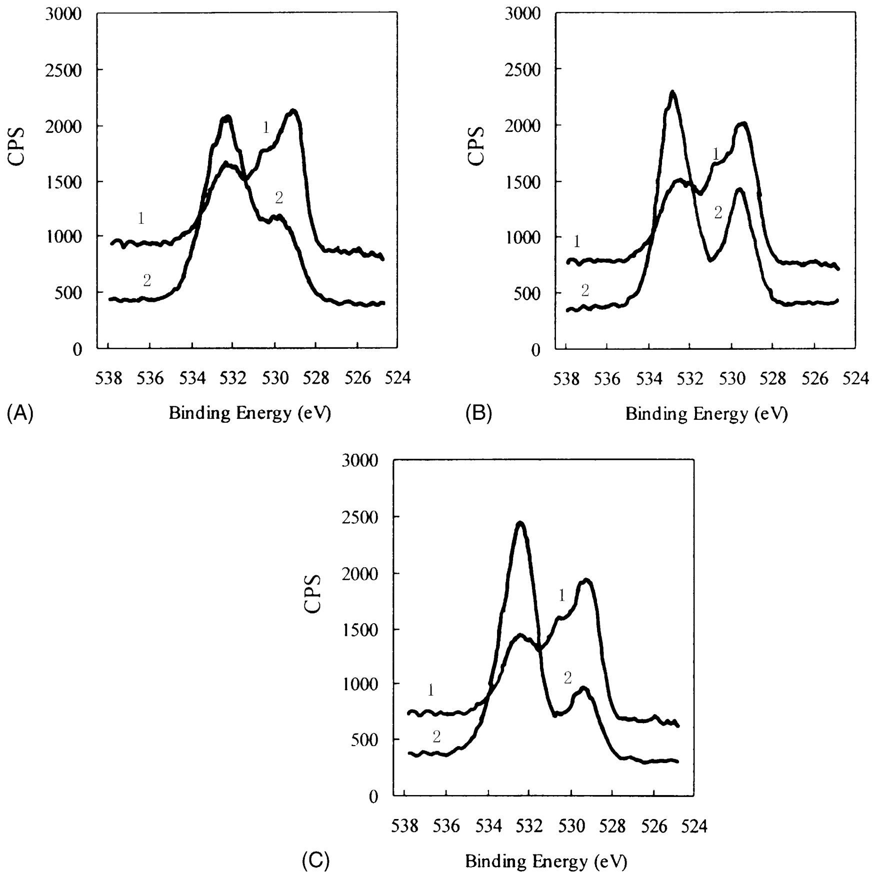

Fig. 2. O 1s photoelectron peak of $Fe/TiO_2/SiO_2$ (A, curve 2), $Co/TiO_2/SiO_2$ (B, curve 2) and $Ni/TiO_2/SiO_2$ (C, curve 2) and TiO_2/SiO_2 (curve 1).

Co and Ni are about 2.00 pH units. The zeta-potential of the modified catalysts is higher than that of the bare one, indicating the surface charges of the former are more positive than the latter, leading to different adsorption behavior. This phenomena could be specified by the above the XPS analysis of the catalysts. The introduction of transition metal resulted in the change of the electronic environment of the lattice titanium. Thus, the surface properties of the catalysts were changed to bring about different photoactivity.

3.2. Adsorption measurements

The equilibrium adsorptions of K-2G and CBX on the surface of different catalysts were investigated. Suspensions were stirred for 30 min in the dark to ensure equilibration of the dyes over the oxide surface, and the amount of adsorption of the dyes on the oxides were tested by comparing the concentration before and after stirring. From Fig. 6, it is observed that the amounts of K-2G adsorbed on transition-metal-supported TiO_2/SiO_2 show higher value

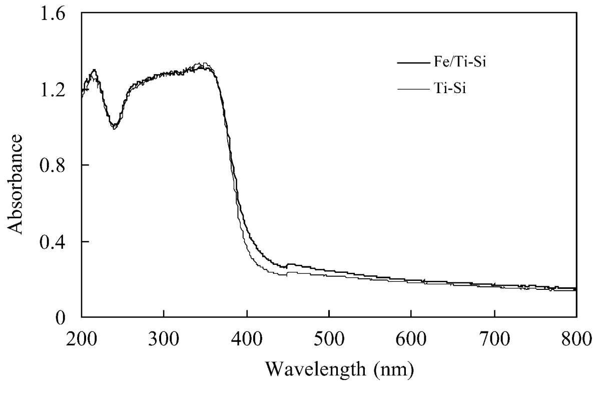

Fig. 3. UV-Vis diffuse reflectance spectra of $Fe/TiO_2/SiO_2$ and TiO_2/SiO_2 photocatalysts.

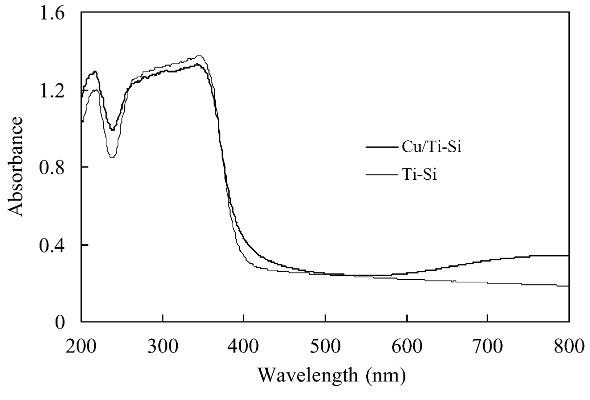

Fig. 4. UV-Vis diffuse reflectance spectra of $Cu/TiO_2/SiO_2$ and TiO_2/SiO_2 photocatalysts.

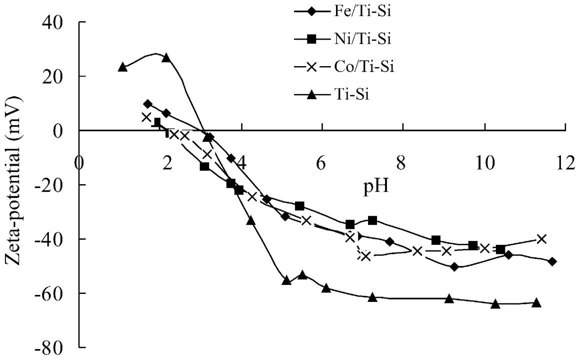

Fig. 5. Plots of the zeta-potential as a function of pH for several photocatalysts suspensions ($0.1\,g\,l^{-1}$) in the presence of KNO_3 (10^{-3} M), respectively. Ti–Si refers to TiO_2/SiO_2 in the figure.

than that on the bare one. Our previous research has verified that K-2G is adsorbed on the surface of TiO_2/SiO_2 by sulfonate group. Based on the XPS and the zeta-potential results, the positive electronic environment of Ti cations of transition-metal-modified catalysts became higher than that of the bare one. The attractive role between sulfonate group and Ti cation increased and caused more adsorption of K-2G on the oxides surface. While CBX was adsorbed on the surface of the catalyst by a positive penta-heterocycle N group. The mode of CBX causes lower adsorption on the positively charged oxide surface due to the repulsive electrostatic power between the oxide surface and adsorbed group. Therefore, the adsorption have a little bit reduction on the modified catalyst. The different adsorption behavior between K-2G and CBX will brought about various photocatalytic efficiency.

3.3. Photocatalytic activity

Fig. 7 showed the results of the photocatalytic degradation of K-2G and CBX over the different transition-metal-supported samples. It is obvious that all transition-metal-doped samples show different reactivity for the both various dyes. For K-2G decolorization, the catalysts modified with Fe, Co and Ni exhibits 2.2–3.3 times higher photocatalytic activity than the bare one, while the photoactivity is suppressed with the addition of Cu^{2+} although $Cu/TiO_2/SiO_2$ has absorption in visible region. On the contrast, only the photoactivity of $Fe/TiO_2/SiO_2$ is 1.68 times higher than TiO_2/SiO_2 for CBX photodegradation, the other modified catalysts have no significant change in the photocatalytic activity. The Fe-doped catalyst shows higher activity for the photodegradation of K-G (2.2 times higher) and CBX (1.68 times higher). The increase in activity is probably due to red shifts. The photocatalytic performance of the other transition-metal-doped catalysts having no significant red shifts predominantly depend on the surface structure properties and reactant. Compared with the adsorption (Fig. 6) and degradation (Fig. 7) results, it is found that the photocatalytic activity is positive correlation to the amount of adsorption over the catalysts generally. The photodegradation rate constants of CBX on most of illuminated modified catalysts are almost the same as that on illuminated bare catalyst because CBX has almost same adsorption on these samples. While these modified samples show higher activity for K-2G photodegradation than the bare one due to the higher adsorption on the former. The results indicate that the amount of substrate adsorbed on the catalyst is an important factor affecting the photocatalytic activity. As well known, the photocatalytic reaction occurs on the surface or near to the catalysts, and recombination of photogenerated electron and hole is very fast, so interfacial charge carrier transfer is possible only when the donor or acceptor is pre-adsorbed before the photocatalytic reaction. The preliminary adsorption of the substrates and the amount of adsorption are very important pre-requisites for highly efficient degradation.

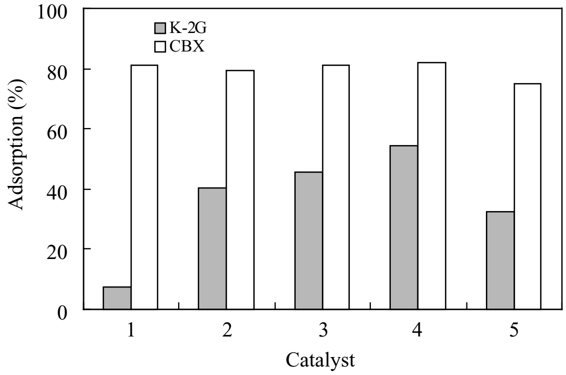

Fig. 6. Adsorptions of K-2G and CBX on the surface of different catalysts: (1) TiO_2/SiO_2; (2) $Fe/TiO_2/SiO_2$; (3) $Co/TiO_2/SiO_2$; (4) $Ni/TiO_2/SiO_2$; (5) $Cu/TiO_2/SiO_2$.

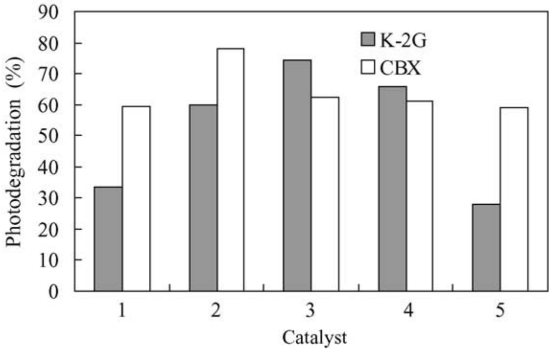

Fig. 7. Photocatalytic degradation rate constants of K-2G and CBX under various illuminated photocatalysts: (1) TiO_2/SiO_2; (2) $Fe/TiO_2/SiO_2$; (3) $Co/TiO_2/SiO_2$; (4) $Ni/TiO_2/SiO_2$; (5) $Cu/TiO_2/SiO_2$.

Also the recombination of photoinduced electron–hole pair is a key factor affecting photoactivity. Based on the XRD results, these metals were uniformly adsorbed on the surface of TiO_2/SiO_2 and may favor separating charge carriers efficiently, prolonging the life of carriers, inhibiting the recombination of electron–hole pairs, and eventually causing the enhancement of the reactivity. In addition, the increased

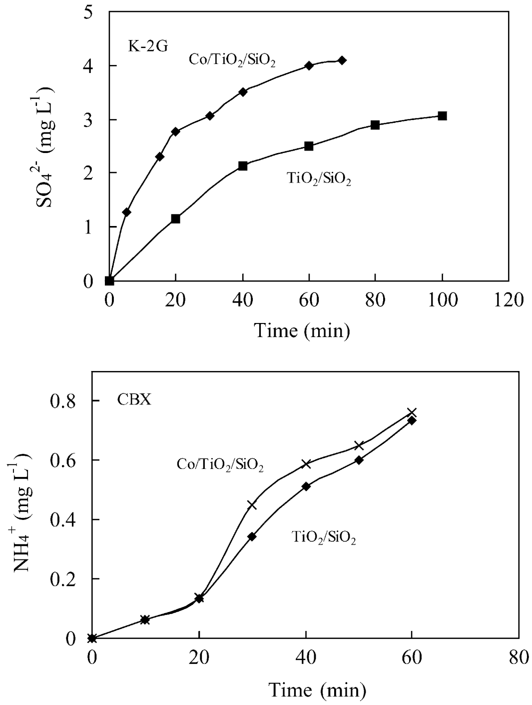

Fig. 8. The formation of SO_4^{2-} ions with exposure time during the photodegradation of K-2G and the formation of NH_4^+ ions with exposure time for CBX photodegradation under illuminated Co/TiO_2/SiO_2 and TiO_2/SiO_2, respectively.

positively electronic of Ti cations with the addition of transition metal lead that more hydroxide ions would be adsorbed onto the surface for charge balance. These hydroxide ions on the surface can accept holes generated by UV irradiation to form hydroxyl radicals, which oxidized adsorbed substrates. Therefore, the photoinduced charge carriers recombination can be suppressed.

3.4. Photodegradation of K-2G and CBX

With the both dyes decolorization, TOC removal and inorganic formation occurred. The SO_4^{2-} ions were followed with exposure time during K-2G photodegradation, while the NH_4^+ ions were followed with irradiation time during CBX photodegradation. The more detail information about the both dyes photodegradation was reported in our previous work [13]. The formation rates of SO_4^{2-} under these catalysts are higher than that in TiO_2/SiO_2 (Fig. 8). The results indicated that desulfuration and decolorization were proceeded simultaneously, and the mineralization rate also increased with the addition of Co. Fig. 8 shows that the amount of NH_4^+ ions produced change under the illuminated samples with reaction time increasing for CBX photodegradation. Obviously, like decolorization, the formation rates of NH_4^+ are almost the same under Co/TiO_2/SiO_2 and TiO_2/SiO_2. It is implied that photocatalytic activity for decolorization and mineralization of dyes could be changed at the same time by the modification transition metal.

4. Conclusions

The introduction of transition metal leads to the changes of the electronic environmental of Ti cations and the zeta-potential of oxides, resulting in different photoactivity from modified and bare catalysts. Photodeposition of Fe, Co, Ni on the surface of TiO_2/SiO_2 enhances photocatalytic activity for the degradation of K-2G by 3.3–2.2 times, in which the rates of decolorization and inorganic ions formation are increased. However, for the photodegradation of CBX, no significant photoactivity increase is observed except Fe modified catalyst. The increase in activity is probably due to the higher adsorption, red shifts, and prevention of electron–hole recombination. The results indicate that the photoactivity could be increased in photodegradation of dyes by changing adsorption of dye onto photocatalyst light absorption of photocatalyst.

Acknowledgements

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