UV Light Induced Photocatalytic Degradation of Cyanides in Aqueous Solution over Modified TiO_2

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Metal doping was adopted to modify TiO_2 (P-25) and enhance the photocatalytic degradation of harmful cyanides in aqueous solution. Ni, Cu, Co, and Ag doped TiO_2 were found to be active photocatalysts for UV light induced degradation of aqueous cyanides generating cyanate, nitrate and ammonia as main nitrogen-containing products. The photoactivity of Ni doped TiO_2 was greatly affected by the state of Ni, that is, the crystal size and the degree of reduction of Ni. The modification effects of some mixed oxides, that is, Ni-Cu/TiO_2 were also studied. The activity of Ni-Cu/TiO_2 for any ratio of Cu/Ni was higher than that of Ni- or Cu-doped TiO_2, and the catalyst at the Cu/Ni ratio of 0.3 showed the highest activity for cyanide conversion.

Keywords : Photocatalytic, Cyanides, TiO_2, Metal doping.

Introduction

Cyanides, in either free or complex form, are very harmful to human being even at very low concentration. So far, great efforts have been made to develop effective methods for treating the industrial waste water polluted by cyanides, including chemical, biological and photocatalytic ways, among which the photocatalytic oxidation process with polycrystalline TiO_2 as catalyst under near UV light radiation is recently appreciated as an attractive method.

Though TiO_2 with crystal structure of anatase or mixture of anatase and rutile has been proved to be effective for degrading versatile organic pollutants in waste water under sunlight or UV light irradiation,[1-3] the modification of TiO_2 for improving its photocatalytic activity is still of vital importance in both theoretical and applied fields. For example, doping of Pt, Ag, ZnO, WO_3, or Fe_2O_3 on TiO_2 surface have been studied.[4-7] Several powdered semiconductors have been reported to be effective for photocatalytic degradation of cyanide, for example, TiO_2, Pt/TiO_2 and ZnO.[8-12] However, there is still an urgent need to develop more stable and highly active photocatalysts. Recently, we discovered that Ni, Cu, Co, and Ag doped TiO_2 are a group of active catalysts for UV light induced degradation of harmful cyanide in aqueous solution, with an extinguished characteristic of producing cyanate, nitrate and ammonia as main nitrogen-containing products.

Experimental Section

The experiments were carried out in a cylinder type Pyrex reactor with an inserted 400W high pressure mercury lamp as UV light source. The reactor was put in a sealed box equipped with thermostatic water bath circulation system. Suspension of reaction liquid and catalyst was vigorously stirred by a magnetic bar. Cyanide (from KCN) concentrations before and after reaction were analyzed by titration with $AgNO_3$ solution using an acetone solution of *p*-dimethylaminobenzylidene rhodanine as an end point indicator. NO_3^- and NH_4^+ were analyzed by a spectrophotometer (Hach DR/2000) and an ammonia selective ion electrode (Orion 93-18), respectively. Cyanate was qualitatively detected by spot-test and in some cases quantitatively analyzed by ion chromatography. M/TiO_2 catalysts were synthesized by conventional impregnation method. Briefly, TiO_2 (P-25) was put into metal nitrate aqueous solution at room temperature with vigorous stirring. After aging, removing water and drying at 110 °C for overnight, the catalyst precursors were ground into fine powder and then calcined at 400 °C for 3 hrs. Each catalyst was finally prepared by reduction of its corresponding oxide in the mixture of H_2 and N_2 (1 : 1) at a desired temperature for 2 hrs. TPR experiments were carried out at a heating rate of 10 $°C \cdot min^{-1}$ with a fixed sample amount of 100 mg.

Results and Discussion

Figure 1 shows the effect of Ni, Cu, Co and Ag loading on the photoactivity of TiO_2. For each run, 300 mL solution containing 1.92×10^{-3} $mol \cdot dm^{-1}$ cyanide and 0.2 g catalyst were used. Metal contents were fixed at 6 wt% for all catalysts unless they were noted. The reaction liquid was carefully filtered and analyzed after 30 min of reaction time. It is obvious that Ni, Cu, Co and Ag loading increase the photoactivity of TiO_2 itself.

Theoretically, the rate of photocatalysis is determined by several factors one of which is the competitive rate of recombination of photogenerated electron-hole pairs within a semiconductor. The presence of surface state at energies inside the band gap region can either decrease or increase the lifetime of electrons and holes depending upon whether these

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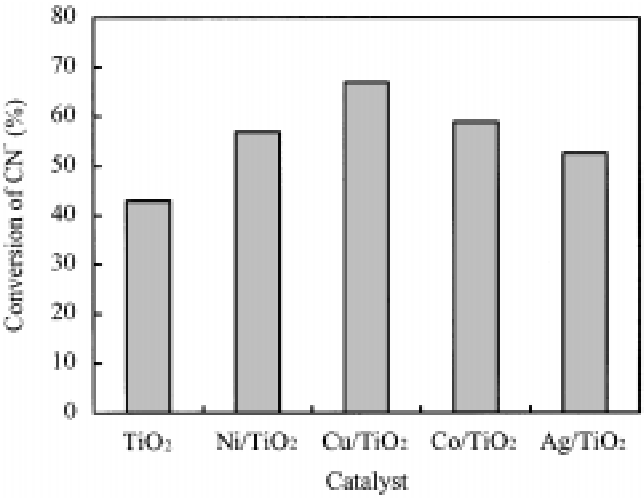

Figure 1. Photoactivity of 3 wt% metal-doped TiO_2 all of which were reduced at 400 °C.

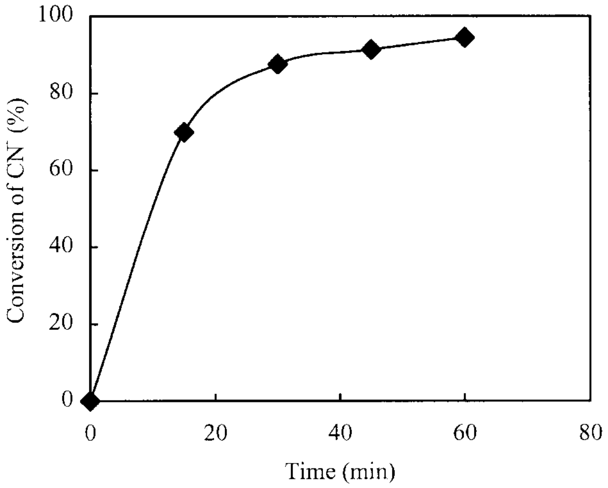

Figure 3. Time dependence of CN^- conversion over Ni/TiO_2 reduced at 500 °C.

energy levels function as efficient recombination centers or as surface traps which prolong the life of holes and electrons. Ni, Cu, Co and Ag are well known as good electron conductors. The existence of those metals on the surface of TiO_2 will help the electron transferring and therefore reduce the possibility of recombination of photogenerated electron-hole pairs, which consequently results in higher photocatalytic activity than that of TiO_2 only catalyst.

Figure 2 shows the thermal stability of TiO_2 upon treatment at different temperatures in the mixture of N_2 and H_2. The contents of anatase (A) and rutile phases in the TiO_2 were calculated from XRD peaks. The content of anatase phase remains constant until the temperature reaches 550 °C indicating that no phase tranfer from anatase to rutile occurs in the range of 400-550 °C.

Figure 3 shows the time dependence of cyanide conversion over Ni/TiO_2 catalyst, which is a typical one for photocatalysis over TiO_2 as reported elsewhere.[10-12] At the initial stage of the reaction, during the first 20 min, the cyanide conversion increases quickly with reaction time. Though the blank tests exclude the possibility of excess contribution of the adsorption of cyanide anion on the Ni/TiO_2 surface, the reaction mechanism is still not clear and the kinetic behaviors deserve further study.

Figure 4 shows the effect of reduction temperature on the activity of Ni/TiO_2 and the relationship between reduction temperature and Ni crystal size. It is obvious that the activity increases as reduction temperature increases in the region of 400 °C-500 °C, and then decreases at higher reduction temperatures. The Ni crystal size greatly increases when the reduction temperature is over 500 °C whereas it increases slightly as reduction temperature increases in the region of 400 °C-500 °C. This suggests that the effect of Ni crystal size on the activity is more favorable than that of surface area. BET surface areas of the catalysts were almost the same one another ranging from 48 m^2/g to 51 m^2/g. Figure 5 shows the TPR curves of NiO/TiO_2 with different loading amounts. The result indicates that there are at least two kinds of NiO species in NiO/TiO_2 system which have different interactions with TiO_2. According to the previous work, our NiO/TiO_2 can be completely reduced to Ni/TiO_2 by mixture

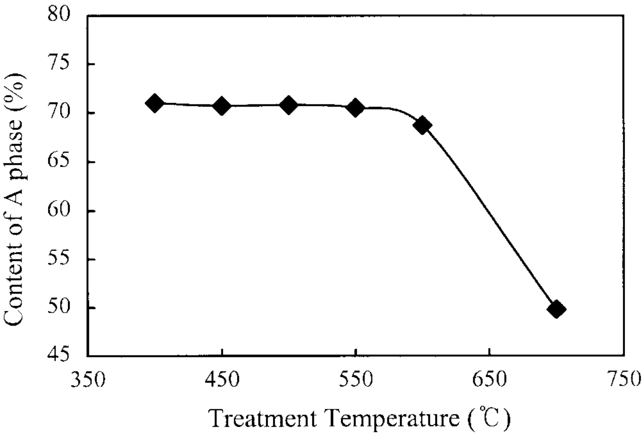

Figure 2. Thermal stability of TiO_2.

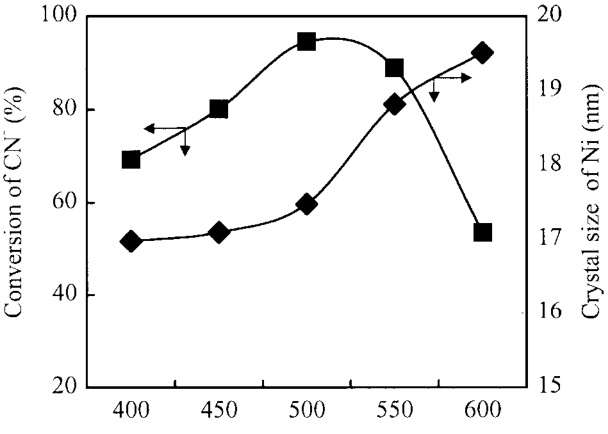

Figure 4. Effect of reduction temperature on CN^- conversion and Ni crystal size over Ni/TiO_2.

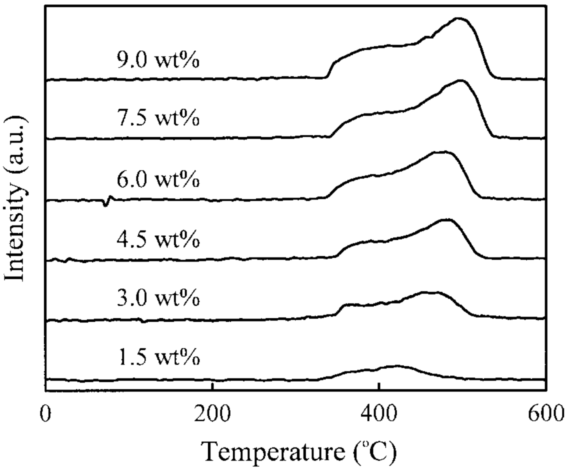

Figure 5. TPR curves of NiO/TiO_2 at different loading amounts.

of nitrogen and hydrogen at the reduction temperature of 500 °C, which is in well agreement with those reported on water splitting.[13,14] At lower reduction temperatures, only part of NiO, surface and isolated ones, can be reduced to Ni metal leaving behind those NiO interacted strongly with TiO_2. Thus, the low activity of the partially reduced catalysts can be reasonably explained by the low content of active Ni metal even though the Ni crystal size on these catalysts is small. At high reduction temperatures, Ni agglomeration occurs resulting in the bigger crystal size, and therefore the lower activity. The best reduction temperature was concluded to be 500 °C.

It has been proved that photogenerated holes oxidize water or adsorbed OH^- species at the surface of a semiconductor to form hydroxyl radicals.[2] These highly reactive radicals can then be used to mineralize or at least partially degrade most organic pollutants to form stable products. At the same time the holes can also react with organic substrates directly to produce organic radicals.[4-10] Since the Ni/TiO_2 catalyst has been well known for hydrogen evolution from water without obvious formation of oxygen, we think metal doping can also promote the *in-situ* formation of hydroxyl radicals which enhance the photoactivity.

The modification effects of some mixed oxides were also studied. In some cases, the reductions of TiO_2 doped with mixed oxides resulted in highly active catalysts. Figure 6 shows the effects of Cu/Ni ratio on the activity of $Ni\text{-}Cu/TiO_2$. All the catalysts were reduced at 500 °C. It is obvious that the activity of $Ni\text{-}Cu/TiO_2$ for any ratio of Cu/Ni is higher than that of Ni- or Cu-doped TiO_2 indicating the synergistic effect of Cu and Ni. The catalyst at Cu/Ni ratio of 0.3 showed a well-developed alloy structure and the highest activity for the conversion of cyanide suggesting that the alloy has better promoting effect than the single metals. Figure 7 shows why a well-developed Ni-Cu alloy forms at Cu/Ni ratio of 0.3. As shown from the dotted lines of Figure 7, the reducibility of Ni was enhanced and that of Cu was reduced as Cu was added suggesting a good compromise of reducibilities of two metals for a good alloy.

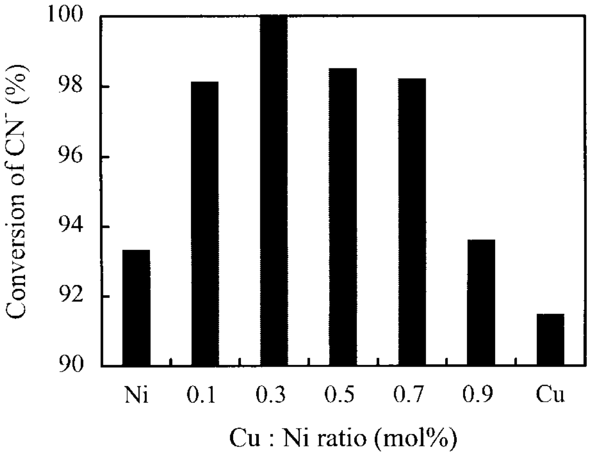

Figure 6. Effect of Cu/Ni ratio on the activity.

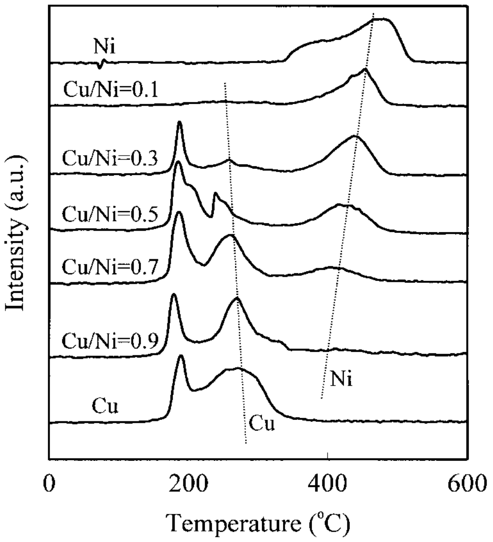

Figure 7. TPR curves of $Ni\text{-}Cu/TiO_2$ at different molar ratios of Cu to Ni.

Different reaction products have been reported over different catalyst. Over ZnO, CO_3^{2-} has been found along with CNO^-,[5] while, over TiO_2, the main products are reported to be CNO^- and NO_3^-.[10] Due to the poor nitrogen mass balance, it was hypothesized that volatile species such NH_3 and N_2 were formed and the volatilization of some part of cyanides as gaseous HCN during the photoreaction might also take place. In our effort of the total analysis of final products by ion chromatography, cyanate, ammonia and nitrate were found to be the main nitrogen-containing degradation products, and a relatively good nitrogen balance, about 80%, was obtained with Ni/TiO_2 catalyst. The loss of nitrogen material balance is probably due to those volatile products, which could not be accurately analyzed in our reaction system. Since leaching problem always exists in the supported metal catalysts in liquid phase reaction, ICP atomic analysis was performed and only small amount of Ni was found in reaction solution even after long time running. XRD confirmed the same ratio of rutile and anatase phase in

Ni/TiO_2 as that in TiO_2 indicating no phase change during the preparation of the catalyst. BET surface area was measured to be about 50 m^2/g. Detailed kinetic and mechanism studies are under going.

Conclusions

Ni, Cu, Co, and Ag doped TiO_2 were found to be active photocatalysts for UV light induced degradation of aqueous cyanides. Cyanate, nitrate and ammonia were analyzed as main nitrogen-containing products and in the case of Ni/TiO_2 catalyst, a relatively good nitrogen balance was obtained. The photoactivity of Ni doped TiO_2 was greatly affected by the state of Ni, that is, the crystal size and the degree of reduction of Ni. The activity of $Ni-Cu/TiO_2$, a mixed oxide doped titania, for any ratio of Cu/Ni was higher than that of Ni- or Cu-doped TiO_2, which meant the synergistic effect of Cu and Ni. The catalyst at the Cu/Ni ratio of 0.3 showed the highest activity for cyanide conversion.

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