Wavelength Effect on Photocatalytic Reduction of CO₂ by Ag/TiO₂ Catalyst

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Abstract: Photocatalytic reduction of CO₂ by water was performed in the presence of a Ag/TiO₂ catalyst under illumination by lamps with different wavelengths (254, 365, and 400 nm). The yields of the main products (methane and methanol) were higher with the 254 nm lamp than with the 365 nm lamp while no products were observed with the 400 nm lamp. This was because the electron-hole generation rate increased with increasing energy of irradiation (decreasing wavelength) and there were higher densities of electron states at higher energies in TiO₂. The increased efficiency of electron-hole generation with a shorter wavelength irradiation increased the efficiency of the catalyst. The energy of the electrons excited by visible light (400 nm) was too low for CO₂ photocatalytic reduction.

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Carbon dioxide emission into the atmosphere is one of the most serious causes of the greenhouse effect. Therefore efforts are made to find effective methods to convert CO₂ into useful compounds. The photocatalytic reduction of CO₂ with H₂O is one of the most desirable and challenging goals in environment protection [1–23].

The semiconductor photocatalytic process is based on the combined use of low energy UV light and a semiconductor photocatalyst, with the anatase form of TiO₂ being the most suitable. In general, photoinduced electrons (e⁻) and positive holes (h⁺) are produced from TiO₂ under the irradiation of UV light ($\lambda < 380$ nm) because this has an energy larger than the band gap (3.2 eV) of TiO₂. The photon flux necessary to initiate these processes can be supplied by sunlight or lamps. Mercury and xenon lamps are the most commonly used lamps to generate UV radiation.

Matthews et al. [24] compared the excitation of TiO₂ under light of wavelengths of 254 and 350 nm. The shorter wavelength radiation of 254 nm was significantly more effective in promoting the photocatalytic oxidation of salicylic acid and phenol. Hu et al. [25] investigated the photodegradation of phenol under UV light at $\lambda < 330$ nm and $\lambda < 200$ nm and reported better results with 200 nm irradiation.

Cao et al. [26] studied photocatalytic degradation of chlorfenapyr using two different monochromatic UV irradiations (300 and 350 nm) and determined that the shorter radiation was more efficient. Jeong et al. [27] evaluated photocatalytic degradation of gaseous toluene using 365, 254 and 254 and 185 nm irradiation in the presence of a TiO₂ catalyst. The highest conversion and mineralization were obtained with 254 and 185 nm light.

Bayarri et al. [28] investigated the wavelength effect in photolysis and heterogeneous photocatalysis. A detailed comparison of the efficiency of UV-A and UV-ABC in photocatalytic and photolytic degradation was done using sulfamethoxazole (SMOX) and 2,4-dichlorophenol (DCP) as model pollutants. It was shown that UV-ABC radiation was more effective than UV-A. Chu et al. [29] evaluated the photocatalytic degradation of dicamba using two different monochromatic UV irradiation (300 and 350 nm). The photocatalysis rate constant was higher with 300 nm irradiation than with 350 nm irradiation. Zhang et al. [30] studied the photocatalytic degradation of pyrene and benzo[a]pyrene (BaP) using UV irradiation wavelengths of 254, 310, and 365 nm. The photocatalytic degradation rates of BaP in the presence of TiO₂ followed the order of 254 nm irradiation

tion > 310 nm irradiation > 365 nm irradiation, while those of pyrene followed the order of 310 nm irradiation > 365 nm irradiation > 254 nm irradiation. Wong et al. [31] studied the photocatalytic degradation of alachlor with different UV lamps (254, 300, and 350 nm). The best quantum yield was obtained with the 300 nm lamp, followed by that at 350 nm and finally at 254 nm. Tan et al. [32] investigated photocatalytic reduction on TiO₂ of CO₂ in the gas phase with different UV lamps. A switching from UVC (253.7 nm) to UVA (365 nm) resulted in a significant decrease in methane yield. This showed that an increase wavelength of UV irradiation significantly decreased the product yield. Tseng et al. [33] performed CO₂ photocatalytic reduction in the liquid phase with different UV lamps (254 and 365 nm) on TiO₂, and observed a similar phenomenon. A switch to UVA (365 nm) resulted in a significant decrease of methanol yield.

The effect of different wavelengths on a Ag-doped TiO₂ on CO₂ photocatalytic reduction performed in the liquid phase with suspended catalysts, and with the products in both phases analyzed, has not yet been studied. The aim of this work is to assess the effect of wavelength (254, 365, and 400 nm) on the photocatalytic reactivity of Ag/TiO₂ exemplified by the photoreduction of CO₂ by water. The photocatalytic reduction of CO₂ in our experiments used a CO₂ saturated liquid phase with suspended Ag/TiO₂ catalyst powder. The products in both the liquid and gas phase were analyzed.

1 Experimental

Pure TiO₂ and silver-enriched TiO₂ powders were prepared by the sol-gel process in a reverse micellar environment. Pure TiO₂ was synthesized by the addition of titanium

(IV) isopropoxide (Ti(OCH(CH₃)₂)₄, Aldrich, 99.999%) into an inverse micellar solution made of cyclohexane (Aldrich, ≥ 99.9%, HPLC grade), non-ionic surfactant Triton X-114 (C₂₇H₄₈O_{7.5}, Aldrich), and distilled water. The molar ratio of cyclohexane:Triton X-114:water: Ti(OC₃H₇)₄ was kept at 11:1:1:1 (volume ratio TX-114:cyclohexane = 0.49). The beaker with the solution made of the appropriate amount of cyclohexane, Triton X-114, and water was stirred vigorously for 15 min for homogenization and formation of inverse micelles. After the addition of all the isopropoxide, the sol was stirred for another 10 min. The sol was left in a bowl exposed to air for 24 h. The rigid gel obtained was calcined at 400 °C for 4 h in an air flow in a muffle furnace. Ag-enriched TiO₂ was similarly prepared, but with using a AgNO₃ (Aldrich, 99.9999%) solution of suitable concentration (1.85 mol/L) instead of distilled water [34].

The crystalline phase of the sample was determined by powder X-ray diffraction (XRD). The specific surface area of catalyst was evaluated by the multipoint BET method from N₂ physical adsorption isotherms. A UV-Vis spectrophotometer was used to record the diffuse reflectance spectra of the sample.

The photocatalytic reduction of carbon dioxide was carried out in a batch stirred annular reactor with suspended catalyst powder illuminated separately by 8 W Hg lamps of 254 and 365 nm and a 8 W Hg lamp filled with argon (400 nm) (Fig. 1). A liquid phase of 0.2 mol/L NaOH and catalyst loading of 1 g/L was used. GC/FID/TCD was used for the analysis of gas and liquid reaction products. The details of the preparation and characterization of the Ag/TiO₂ catalyst, and descriptions of the photocatalytic CO₂ reduction experiment and analytical methods have been previously described [34,35].

Fig. 1. Schematic of the apparatus for CO₂ photocatalytic reduction.

2 Results and discussion

The textural properties and absorption edge of the prepared pure TiO₂ and Ag-doped titania are given in Table 1, together with the actual Ag content. The samples had a relatively high surface area, and the positive effect of silver was evident. XRD analysis confirmed the presence of anatase structure while Ag was not detected, which indicated that Ag was present as metallic clusters inside the TiO₂ powder. The UV-Vis spectra of the catalysts showed an absorption shift to the visible region for the Ag/TiO₂ catalysts [34].

Table 1 Characterization data of the prepared samples

Sample	Ag content (wt.%)	<i>A</i> _{BET} (m ² /g)	Pore size <i>r</i> _{max} (nm)	Absorption edge (eV)
TiO ₂	0.00	67.6	1.48	2.98
Ag/TiO ₂	5.19	79.7	1.65	2.74

The effect of irradiation time on the formation of CO₂ photocatalytic reduction products was investigated with various wavelengths of radiation for periods of 0–24 h. Two main products were obtained, which were methane in the gas phase and methanol in the liquid phase. Hydrogen and low amounts of carbon monoxide were also detected. Other products such as formic acid, formaldehyde, ethane, and ethylene could also be formed [14] but they were not detected. Methane and methanol produced versus irradiation time with wavelengths of 254, 365, and 400 nm for the Ag/TiO₂ catalyst are shown in Fig. 2 and 3.

A substantial increase of methane yield was observed after 8 h of irradiation with the 254 nm lamp on the Ag/TiO₂ catalyst (Fig. 2). The methane yield over the pure TiO₂ catalyst with the 254 nm lamp was markedly less than over Ag/TiO₂.

The yields of methane were significantly lower with the 365 nm lamp than with the 254 nm lamp and the values obtained were almost the same for the two catalysts.

Fig. 2. Time dependence of CH₄ yield over pure TiO₂ and Ag/TiO₂ catalysts irradiated by lamps with various wavelength.

Fig. 3. Time dependence of CH₃OH yields over the pure TiO₂ and Ag/TiO₂ catalysts irradiated by lamps with various wavelength.

The yields of methanol with the 400 nm lamp were one order of magnitude lower than the yields of methane over the Ag/TiO₂ catalyst (Fig. 3). Data at 5 h were measured but these were below the limit of detection (12 μg/L or 0.38 μmol/g). The yields of methanol for the shorter radiation wavelength were higher and comparable with the yield of methane. Therefore CH₃OH yields for the 400 nm lamp for both methane and methanol were not measured.

Pure TiO₂ has a relative large energy band gap and can only be excited by high energy UV irradiation with a short wavelength (UVA). Efforts have been made to extend the light absorption range of TiO₂ from UV to visible light by adding noble metals. In this work the material used (Ag/TiO₂) has an absorption edge of 2.74 eV, so this catalyst was expected to be active with irradiation of a longer wavelength Vis or at least UVC. Unfortunately, electrons excited by visible light do not have sufficient energy for the photocatalytic reduction of CO₂ since the Ag energy levels were probably under the TiO₂ conduction band edge. The increased activity of TiO₂ with incorporated Ag [34] was probably not caused by a decreased absorption edge, but the more probable reason was a decreased carrier recombination rate due to the spatial separation of electrons and holes in the surrounding Ag clusters. The Ag content of 5.2% comprised silver atoms that were not randomly located in the TiO₂ crystal, but that probably formed metallic clusters inside the TiO₂ powder [34]. These metal clusters would cause a decrease in the electron-hole recombination rate [36–40]. The Fermi level of TiO₂ is higher than that of silver metal [41].

Some works have shown that the composite of two kinds of semiconductors or two phases of the same semiconductor was beneficial in reducing the recombination of photogenerated electrons and holes, and thus enhanced photocatalytic activity. The interface between the two phases probably act to rapidly separate the photogenerated electrons and holes due to the difference in the energy levels of their conduction

bands and valence bands [42–44].

The electron-hole generation rate increased considerably with increasing energy of irradiation (i.e. decreasing wavelength) due to the higher densities of electron states at higher energies in TiO₂ [45,46]. The increased efficiency of electron-hole generation increased the efficiency of the catalyst when a shorter wavelength irradiation was used. Our results are in agreement with other works on CO₂ photocatalytic reduction on TiO₂ catalyst initiated by UV sources with different wavelengths [32,33].

3 Conclusions

The photocatalytic reduction of CO₂ in the presence of Ag/TiO₂ and TiO₂ catalysts under separate illumination by lamps of 254, 365, and 400 nm wavelength was studied. The radiation with the shorter wavelength of 254 nm was significantly more effective for CO₂ photoreduction than the 365 nm radiation, which was expected to be better from the Ag/TiO₂ band gap (2.74 eV). The increased efficiency of electron-hole generation with the shorter wavelength of irradiation increased the efficiency of the catalyst. The radiation with the wavelength of 400 nm was not effective at all, probably because the energy of electrons excited by visible light (400 nm) was too low for CO₂ photocatalytic reduction.

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