JOURNAL OF MATERIALS SCIENCE **34** (1999) 4089–4093

Modification of titania particles by ultrasonic spray pyrolysis of colloid

JONG HO LEE, KYEONG YOUL JUNG, SEUNG BIN PARK*
Department of Chemical Engineering, Korea Advanced Institute of Science and Technology, 373-1, Kusong-dong Yusong-gu, Taejon 305-701, Korea
E-mail: sbpark@lamp.kaist.ac.kr

Composite fine particles such as ZnO-TiO_2, CdS-TiO_2, ZnS-TiO_2 and Ag-TiO_2 were prepared by ultrasonic spray pyrolysis of metal salt aqueous solution in which TiO_2 (Degussa P25) particles were suspended. The crystallinity, chemical compositions, and morphologies of the produced particles were investigated by XRD, centrifugal particle size analyzer, and SEM/EDAX. The photocatalytic activity of the modified particles was investigated for the decomposition of trichloroethylene (TCE). The prepared particles were micro-porous and had spherical shapes of 0.3–1.5 μm in diameter. The size and size distribution of the prepared particles were not significantly changed by the type and loading of modifier. The crystallinity and crystallite size of TiO_2 was not changed by these modifications. The photocatalytic activities of modified particles was slightly higher than pure titania when the loading was low. However, as the loading was further increased, the photocatalytic activity was sharply decreased and became almost constant.

1. Introduction

Recently, the preparation of ultrafine particles by spray pyrolysis of colloidal particles in a precursor solution has been studied [1–6]. This method is applicable for drying of colloids, direct control of microstructure and size of particles, and control of composition in particles. When the precursor solution is atomized to form droplets and pyrolyzed, the colloidal particles serve as seeds for nucleation. Thus the dense particles are easily formed.

Ortega and Kodas [2] added the colloidal seed particles in order to prevent particles from becoming hollow and porous. Moore *et al.* [3] prepared mullite powder ($3Al_2O_3 \cdot 2SiO_2$) by spray pyrolysis of aluminum nitrate aqueous solution with suspended fumed silica. They reported that the prepared particles were not strongly agglomerated and their mean size was about 0.6 μm. Ohshima *et al.* [4] prepared ZnO-TiO_2 composite particles by ultrasonic spray pyrolysis of the $Zn(NO_3)_2$ aqueous solution with suspended TiO_2 particles. The prepared composite particles ranged from 0.36 to 0.5 μm in size and they had better UV absorption characteristics than that of pure ZnO and TiO_2 particles. Matijevic *et al.* [5] reported that droplets were completely converted to particles by injecting AgCl nuclei into carrier gas when silica/titania composite particles were prepared by spray pyrolysis of tetraethyl orthosilicate and titanium(IV) ethoxide. Kang *et al.* [6] reported that γ-$LiAlO_2$ particles, which had pure crystalline phase and high surface area, were prepared by ultrasonic spray pyrolysis of a colloidal mixture of alumina sol and lithium salt. The particles prepared from the colloidal mixture had rough surfaces and high surface area (45 m^2/g), due to the heterogeneous precipitation of the lithium component on the fibrils of the aluminum hydroxide sol, while the particles prepared from the aqueous solution had smooth and low surface area (7 m^2/g).

In this paper, the surface composition of titania particles was changed by ultrasonic spray pyrolysis of various metal salt aqueous solutions in which titania particles (Degussa P25) were suspended.

2. Experimental

2.1. Spray drying of pure TiO_2 (Degussa P25)

In order to evaluate the characteristics of spray pyrolysis of colloid, spray drying of pure TiO_2 (Degussa P25) suspension was performed. The spray solution was prepared by suspending TiO_2 particles in water, and then it was sonicated for 5 min in order to obtain good dispersion. The concentration of suspended titania particles was 7.8 g/l. This solution was spray-dried by using the ultrasonic spray pyrolysis apparatus as shown in Fig. 1. The reactor has the length of 50 cm, the inner diameter of 2.5 cm, and the outer diameter of 3 cm. The ultrasonic nebulizer (SAMSUNG Co. HU-45301B) has the frequency of 1.67 MHz and the liquid depth of 3 cm. The temperature of the furnace reactor was maintained at 550 °C and nitrogen was used as carrier gas. The flow rate of carrier gas was 5 l/min and the residence time in reactor was 3 sec. The production rate of the modified titania was 0.1 g/h for the current experimental conditions.

---

[*] Author to whom all correspondence should be addressed.

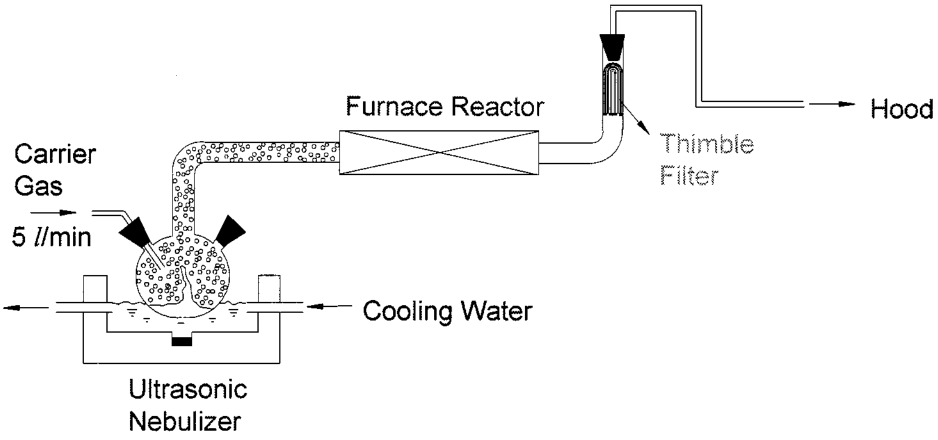


Figure 1 The ultrasonic spray pyrolysis system.

2.2. Preparation of ZnO-TiO_2 and Ag-TiO_2 composite particles

Solutions were prepared by dissolving $Zn(NO_3)_2$ (0.2, 0.05, 0.02 and 0.005 M) or $AgNO_3$ (0.2, 0.02 M) in water, in which TiO_2 particles (Degussa P25) were later added. These solutions were sonicated for 5 min. The concentration of suspended TiO_2 particles was fixed at 7.8 g/l. ZnO-TiO_2 or Ag-TiO_2 composite particles were prepared by ultrasonic spray pyrolysis of these spray solutions. The temperature of furnace reactor was maintained at 550 °C and nitrogen gas was used as carrier gas. The flow rate of carrier gas was 5 l/min.

2.3. Preparation of ZnS-TiO_2 and CdS-TiO_2 composite particles

The solution were prepared by dissolving $Zn(NO_3)_2$ or $Cd(NO_3)_2$ and thioacetamide (TAA) in water solvent, in which TiO_2 particles (Degussa P25) were later added. These solutions were sonicated for 5 min. The concentration of suspended TiO_2 particles was 7.8 g/l and the concentration of $Zn(NO_3)_2$ and TAA were 0.08 and 0.2 M, respectively, when the ZnS-TiO_2 composite particle was prepared. The concentrations of $Cd(NO_3)_2$ and TAA were 0.02 M for the preparation of CdS-TiO_2 composite particles. ZnS-TiO_2 and CdS-TiO_2 composite particles were prepared by ultrasonic spray pyrolysis of these solutions. The temperature of furnace reactor was maintained at 150 °C when the ZnS-TiO_2 composite particle was prepared, and 370 °C when the CdS-TiO_2 composite particle was prepared. The high temperature is not required, which is lower than that of the preparation of ZnO-TiO_2 or Ag-TiO_2 composite particles, since $Zn(NO_3)_2$ or $Cd(NO_3)_2$ and TAA are rapidly converted to ZnS and CdS precipitate at low temperature. Nitrogen gas was used as carrier gas and the flow rate of carrier gas was 5 l/min.

2.4. Characterization of prepared composite particles

The crystalline phase and crystallinity of the composite particles were investigated by X-ray diffraction (XRD; RIGAKU, D/MAX-RB, CuK_α, 4 deg/min). The compositions of modified particles were determined by EDAX(SEM). The morphology and size of particles were observed from scanning electron microscopy (SEM; Philips, 535M) and measured by centrifugal particle size analyzer (CPSA; Shimadzu, SA-CP3).

The photocatalytic activities of modified particles were measured for the decomposition reaction of trichloroethylene (TCE) by the photocatalytic reaction system shown in Fig. 2.

$$C_2HCl_3 + \tfrac{3}{2}O_2 + H_2O \rightarrow 3HCl + 2CO_2 \qquad (1)$$

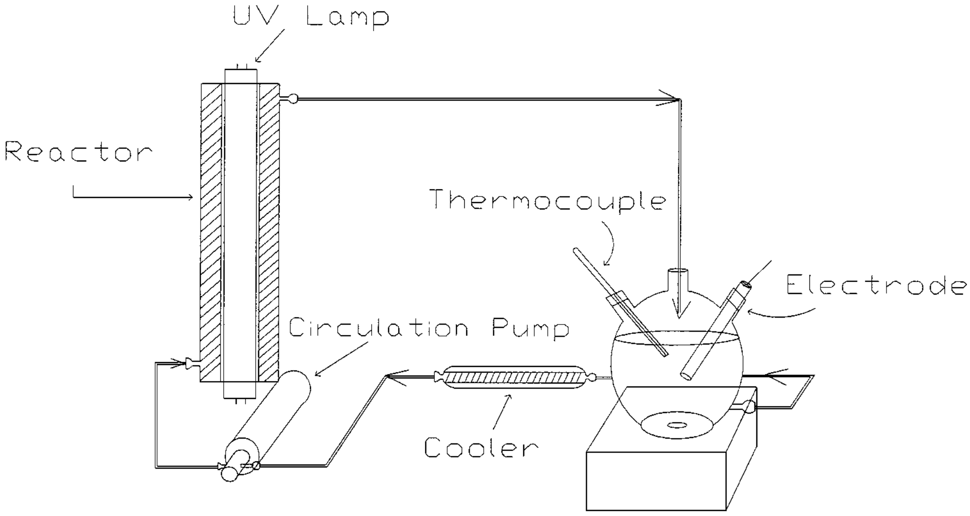


Figure 2 The photocatalytic reaction system.

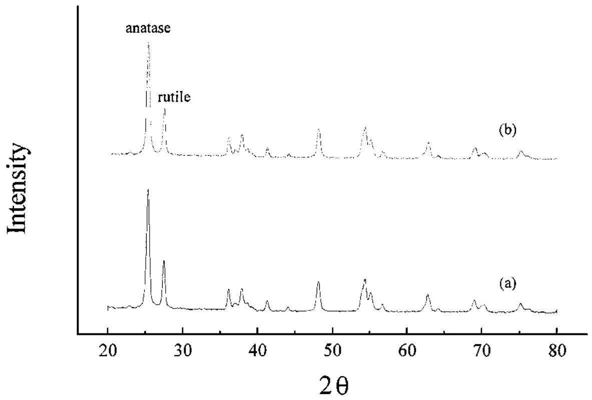


Figure 3 X-ray diffraction patterns of (a) TiO_2 (Degussa P25) and (b) spray dried TiO_2.

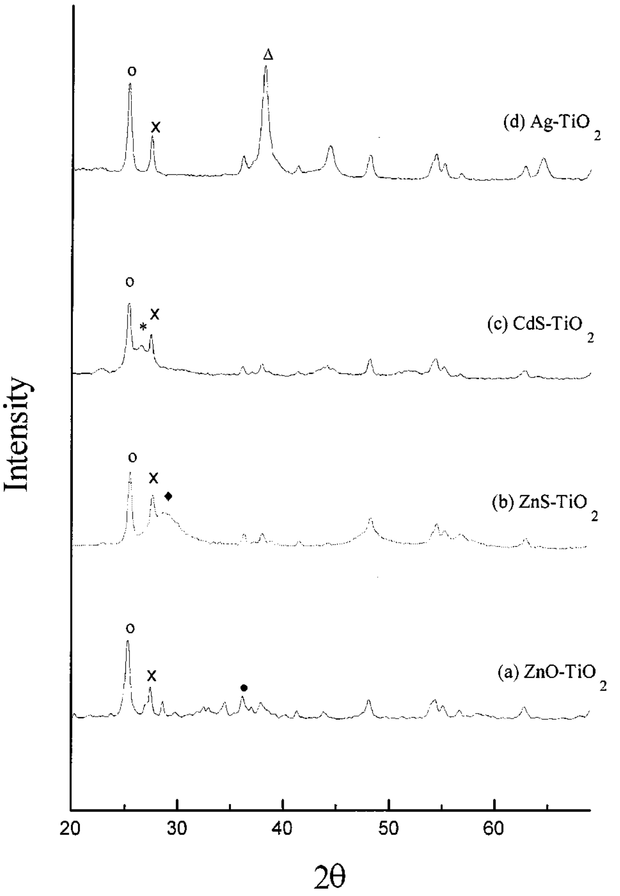


Figure 4 X-ray diffraction patterns of modified titania particles: 0: TiO_2(anatase), ×: TiO_2(rutile), ●: ZnO, ♦: ZnS, *: CdS, Δ: Ag.

The irradiation wave length of the UV lamp ranged from 300–420 nm, and the average wave length was 350 nm. The initial TCE concentration was fixed at 58.56 ppm. The decomposition rate of TCE was measured by monitoring the concentration of Cl^- ion in the solution by using Cl^- electrode (Orion, Model 96-17B).

3. Results and discussion

XRD spectra of TiO_2 (Degussa P25) particles and TiO_2 particle prepared by spray drying of colloidal TiO_2 are shown in Fig. 3. The two XRD patterns are identical. Therefore, the crystallinity of TiO_2 was not changed at the temperature under 550 °C by the spray drying/pyrolysis system shown in Fig. 1. This is also confirmed from XRD spectra of modified TiO_2 particles (shown in Fig. 4). Both characteristic peaks of anatase and rutile are shown in Figs 3 and 4. Also, Fig. 4 indicates that the crystals of ZnO, ZnS, CdS and Ag were successfully formed in the modified particles.

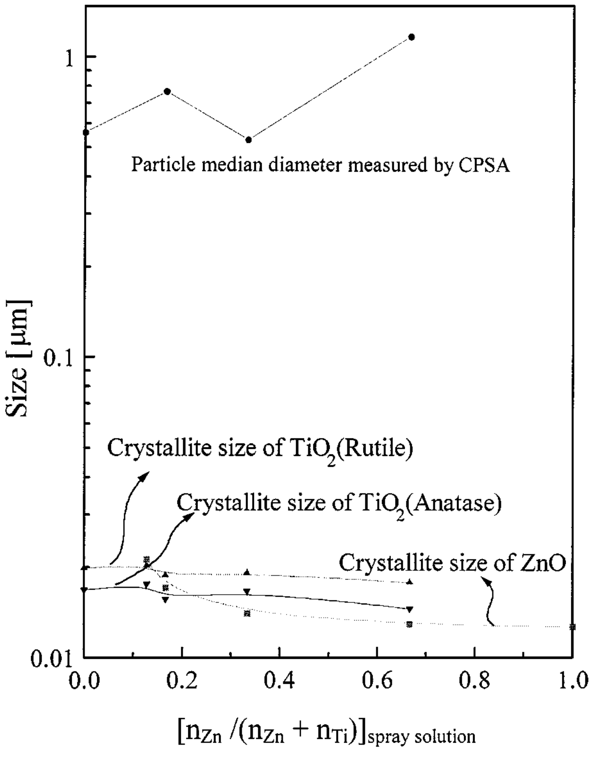
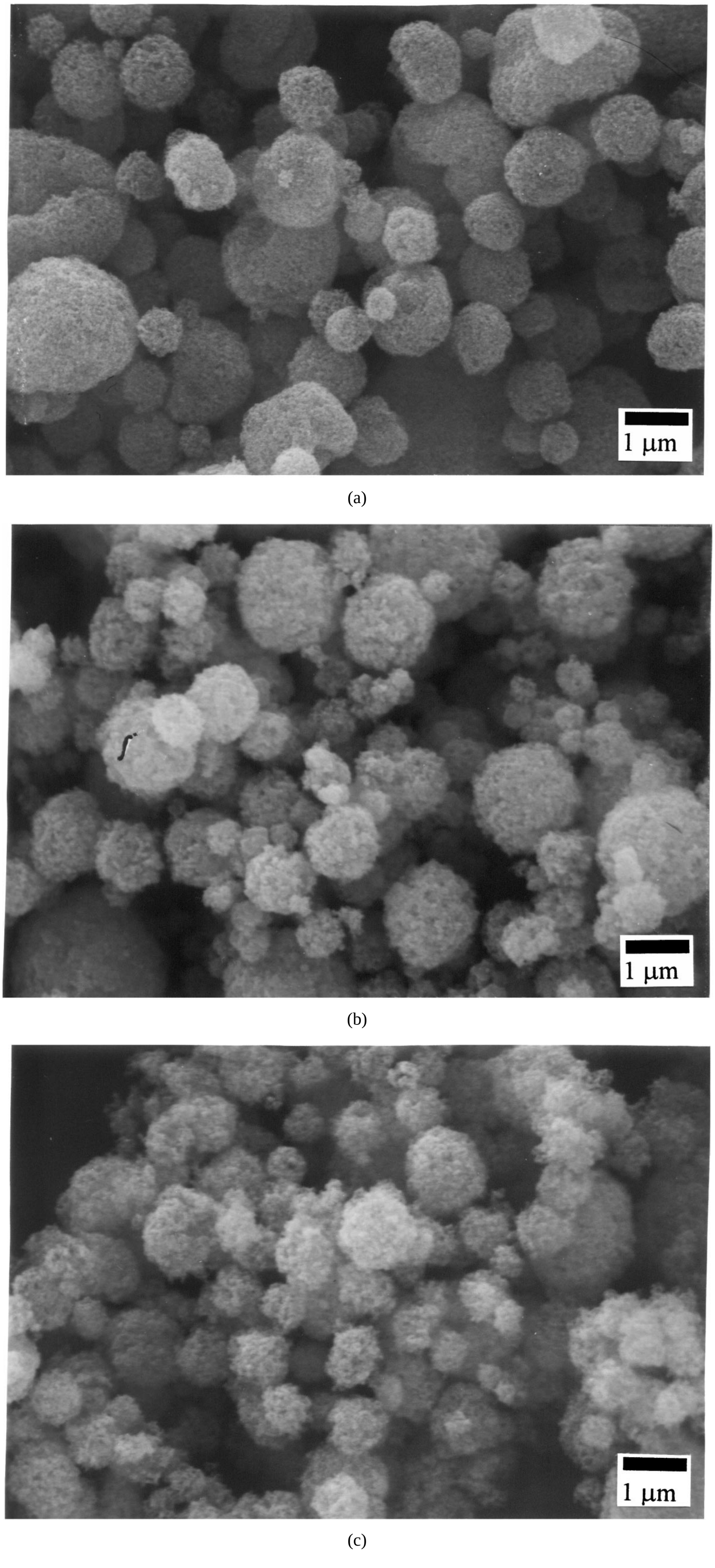


Figure 5 The median diameters of ZnO-TiO_2 composite particles measured by centrifugal particle size analyzer and the crystallite size of ZnO and TiO_2.

The median diameter of ZnO-TiO_2 composite particles was measured by CPSA. The crystallite sizes of TiO_2 (anatase, rutile) and modifier were calculated from XRD patterns with the loading of modifier. Fig. 5 shows the median diameter and the crystallite size of the prepared composite particles. The particle median diameter and crystallite size of TiO_2 did not change significantly with the loading of ZnO. However, the crystallite size of ZnO was decreased slightly. It was also confirmed that the crystallinity of TiO_2 was not changed by this spray pyrolysis system.

Fig. 6 shows SEM photographs of spray dried titania particle and modified particles. Prepared particles are spherical and micro-porous aggregates. This figure shows that the primary particles of the modified particle are larger than the spray dried titania, and the modified particles are more porous. From these results, it is clear that the modifier is precipitated and pyrolyzed on the surface of the titania particle. The particle size ranged from 0.3 to 1.5 μm. Regardless of the types of modifiers, the particles had similar shape and size.

The extent of ZnO formation in the prepared ZnO-TiO_2 composite particle was tested by measuring the Zn fraction in the particle by EDAX(SEM). Fig. 7 shows that all $Zn(NO_3)_2$ in solution was converted into ZnO in the composite particle. This implies that the composition of the modified particles can be directly



(a)

(b)

(c)

Figure 6 SEM photographs of produced particles: (a) Spray dried TiO_2 ($C_{TiO_2} = 7.8$ g/l); (b) CdS-TiO_2; (c) Ag-TiO_2 ($C_{AgNO_3} = 0.02M$).

controlled by changing the composition of spray solution.

The effect of modifier loading on the photocatalytic activity for the decomposition of TCE is shown in Fig. 8. The photocatalytic activity was slightly higher than that of pure titania when the modifier loading is low. As the modifier loading is further increased, the photocatalytic activity is sharply decreased and becomes almost constant, which lies between pure TiO_2 and pure ZnO in case of ZnO-TiO_2 composite particle. From this result, it is concluded that the initial surface modification determines the photocatalytic activity and the further modification does not affect the chemical property.

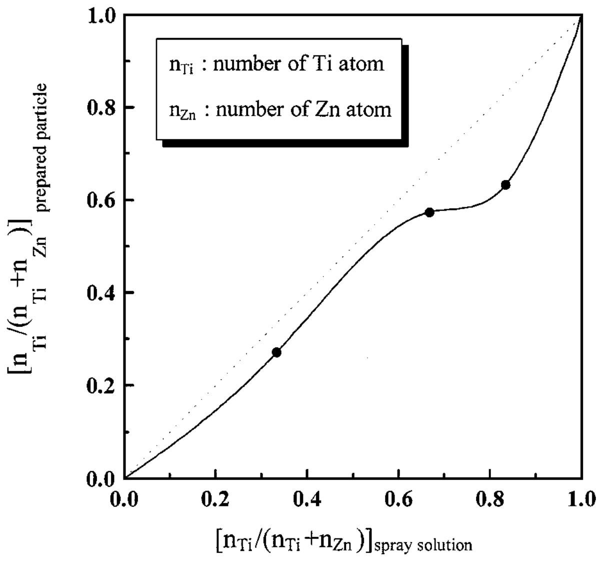


Figure 7 The relationship between the composition of spray solution and the composition of prepared particle.

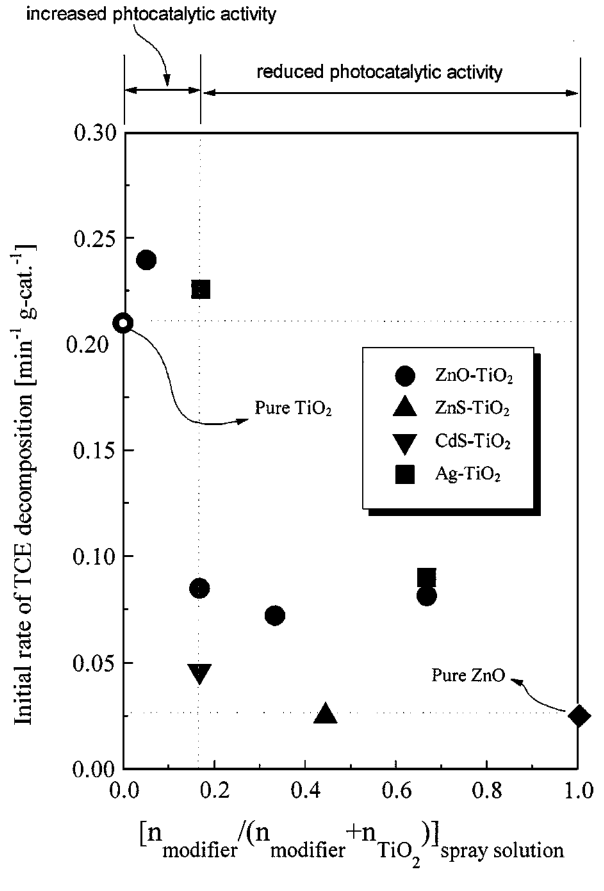


Figure 8 The photocatalytic activities of modified particles with changing the modifier loading.

4. Conclusions

The properties of titania particles were modified by ultrasonic spray pyrolysis of metal salt aqueous solution in which titania particles suspended. Prepared ZnO-TiO_2, ZnS-TiO_2, CdS-TiO_2 and Ag-TiO_2 composite particles were spherical and micro-porous aggregates. These modified particles had sizes ranged from 0.3 to 1.5 μm when the concentration of TiO_2 suspended in spray solution was 7.8 g/l, and their size and size distribution were not significantly changed by changing the type of modifier or the loading. The crystallite size of modified particle was 10–20 nm and the crystallinity of TiO_2 was not changed by this modification process. The photocatalytic activities of modified particles are slightly higher than pure titania when the loading is low ($\sim$0.15 mol %), however, as the loading is further increased, the photocatalytic activity is sharply decreased and becomes almost constant. These results demonstrate that the surface modification of colloidal particles can be modified by ultrasonic spray pyrolysis.

Acknowledgement

This paper was supported by Non Directed Research Fund, Korea Research Foundation (1994–1995).

References

1. Y. KOUSAKA, T. HORIUCHI, Y. ENDO and S. AOTANI, *Adv. Mat.* **6** (1989) 180.
2. J. ORTEGA and T.T. KODAS, *J. Aerosol Sci.* **23** (1992) S253.
3. K. A. MOORE, J. CESARANO III, D. M. SMITH and T. T. KODAS, *J. Amer. Ceram. Soc.* **75** (1992) 213.
4. K. OHSHIMA, K. TSUTO, K. OKUYAMA and N. TOHGE, *Aerosol Science and Technology* **19** (1993) 468.
5. E. MATIJEVIC, Q. ZHONG and R. E. PARTCH, *ibid.* **22** (1995) 162.
6. Y. C. KANG, S. B. PARK and S. W. KWON, *J. Colloidal and Interface Sci.* **182** (1996) 59.

Received 2 January 1997
and accepted 7 December 1998