Effect of Quenching Medium on Photocatalytic Activity of Nano-sized TiO_2 Prepared by Solvothermal Method

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Introduction

Titanium dioxide (TiO_2) is an attracted material since it can be used in catalytic reactions acting as a promoter, a carrier for metals and metal oxides, or as a photocatalyst etc. [1]. Nano-sized TiO_2 has been successfully prepared by several methods. Based on those preparation methods, many papers reported that the photocatalytic activity of nano-sized TiO_2 is sensitively by particle size, specific area, crystalline phase and surface properties (e.g. surface OH and oxygen vacancy) [2]. Besides improvement the photocatalytic activity of the TiO_2 catalyst during preparation, pre-treatment processes were used to modify characteristics of synthesized TiO_2. It is known that surface defects play an important role in the photocatalytic activity, since defects act as active sites for the adsorption and dissociation of molecules on the surface [3]. The variety of the surface defects, strains and reconstructions caused by the process of quenching [4]. Therefore, quenching process is an effective pre-treatment method for improve photocalytic activity of the TiO_2

Experimental

Nano-sized TiO_2 powders were synthesized by solvothermal method at 573 K for 2 h using titanium *n*-butoxide (97 %, Aldrich) as the precursor in toluene medium. The obtained TiO_2 was heat treated in air atmosphere at 573 K for 1 h and then it was taken out and immediately quenched in various media. After the samples were quenched, all samples were stored in a desiccator. These samples were characterized by XRD, BET, CO_2-TPD, and XPS analysis. The photocatalytic activity of TiO_2 photocatalyst was evaluated by measuring decomposition rates of ethylene UV conditions. All the experiments were carried out using horizontal quartz fixed bed reactor. The weight of the catalyst was kept constant at 0.4 g. The reactor was placed in a closed stainless box at top of which a 500 W mercury lamp (Philips, HPL-N) was provided, emitting in the UV light region. High purity grade air containing 0.1 vol.% ethylene was continuously fed at a constant flow rate with GHSV of 120 h^{-1}. The outlet gas was taken every 30 minutes and its composition was analyzed using a Shimadzu GC14B (VZ-10) gas chromatograph equipped with the flame ionized detector.

Results and Discussion

Characteristics and photocatalytic activity of TiO_2 samples were shown in Table 1. The XRD spectra show the characteristic peaks of anatase phase (major peak: 25.30, 37.80, 48.14°). The BET surface area data of quenched TiO_2 are in the range of 87-112 m^2g^{-1}. On the survey, XPS scan signals originating from O 1s, Ti 2p and C 1s are easily identified at binding energies around 530, 464 and 285 eV, respectively. The XPS Ti 2p spectra could be fitted with Gaussian-Lorentzian functions into three spin-orbit components at binding energies 455.5, 457.2 and 459.2 eV and were identified with TiO (Ti^{2+}), Ti_2O_3 (Ti^{3+}) and TiO_2 (Ti^{4+}) fractions in the particle [5], respectively. Additionally, based on CO_2-TPD technique [6] shown that the amounts of surface Ti^{3+} defect sites on the TiO_2 samples were observed from the areas under the Ti^{3+} TPD peaks and were found to be in the following order: air at 77 K > H_2O_2 at RT > H_2O_2 at 373 K > H_2O at RT > H_2O at 373 K > liquid N_2 > air at RT. The percentage conversion of ethylene decomposition as amount of surface Ti^{3+} is shown in Fig.1. It showed that the more there are Ti^{3+} on the surface of TiO_2, the better the photo-catalytic activity displayed.

Table 1. Structural properties of TiO_2 synthesized by solvothermal method after quenching in various media

Quenching medium	Crystallite size (nm)	S_{BET} (m^2/g)	Surface Ti^{3+} (%)	Conversion (%)
Liquid N_2	10.8	87	7.9	24.5
H_2O at RT	10.4	112	8.7	27.8
H_2O at 373 K	10.5	94	8.1	26.0
H_2O_2 at RT	13.3	94	8.9	32.5
H_2O_2 at 373 K	13.2	90	8.8	31.8
Air at RT	10.6	93	7.4	21.6
Air at 77 K	10.6	97	9.4	34.6

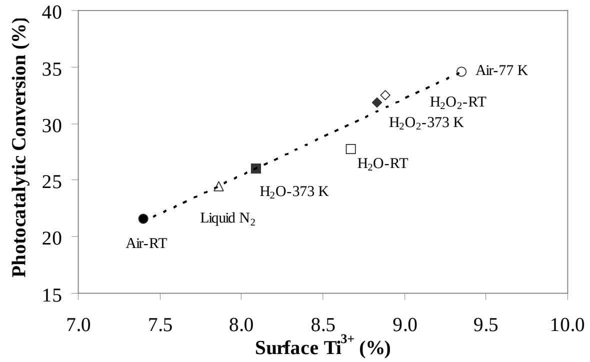

Figure 1. Percentage of decomposed ethylene vs. amount of surface Ti3+ sites of TiO_2 samples quenched in different media.

References

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