

Research Article

Investigation of Oxygen Adsorption Property of Partially Reduced ${\rm Tio}_{_2}$ (Tio_-X)

YoonKuen Chae¹, Shinsuke Mori², Masaaki Suzuki² and JinWon Park^{1*}

¹Department of Chemical and Biomolecular Engineering, University of Yonsei, 262 Seongsanno, Seodaemun-gu, Seoul 120-749, Korea ²Department of Chemical Engineering, Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro-ku, Tokyo, 152-855

Abstract

The partial reduction of TiO₂ was investigated by hydrogen plasma treatment and it was performed to examine the oxygen adsorption property of partially reduced TiO₂ (TiO_{2-x}). In this experiment, TiO_{2-x} was analyzed by X-ray diffraction (XRD) and oxygen adsorption of partially reduced TiO₂ (TiO₂ was measured by gas chromatography (GC). Consequently, it was shown that hydrogen plasma treatment can partially reduce TiO₂ by plasma effects and TiO_{2-x} can adsorb oxygen. The H₂O formation and the oxygen adsorption were found to be dependent on the heating temperature. The oxygen adsorption property was attributed to the formation of Ti₂O₃.

Keywords: Hydrogen plasma; Reduction; TiO_2 ; Oxygen adsorption; Ti_2O_3 .

Introduction

Plasma treatment was applied to the reduction of metallic oxide [1,2]. The reduction of metallic oxide has been examined using low pressure plasma containing hydrogen via radio-frequency, microwave, photochemical or electrochemical methods and heating [3-5]. Titanium dioxide (TiO_2) , a representative metallic oxide, is especially attractive for environmental applications because of its chemical stability, non-toxicity and other advantageous properties. As a result, it has become by far the best-characterized oxide material. It is used in heterogeneous catalysis such as a photocatalyst in solar cells for the production of hydrogen and electric energy and as a gas sensor [6-11]. In addition, it is expected to remove a fetor through oxygen adsorption by the partially reduced TiO₂ in this study.

In heterogeneous catalysis, interaction of TiO₂ surface with oxygen (O_2) is necessary. The chemistry of oxygen is an important, but often overlooked, component of many chemical and photochemical processes that take place on TiO2-based materials. Oxygen is widely used in photochemical oxidation studies on TiO, and is usually considered to act primarily as a scavanger of the photoexcited electrons, thus preventing negative charge accumulation on the surface of catalyst. In some solution-phase photochemical studies, the resulting superoxide radical anion (O_{2}) species are envisioned to participate in homogeneousphase reactions with water molecules to form hydrogen peroxyl species that may play a role in organic oxidation, either in solution or on the surface. Only a few groups have proposed that surface-bound O₂ or O₂⁻ species may be directly involved in photooxidation of coadsorbed species. The step of O_2^{-1} formation upon chemisorption of oxygen requires the presence of surface vacancy sites. No oxygen adsorption would occur on a stoichiometric surface. However, the exact nature of adsorbed O₂ on these TiO₂ surfaces is not well understood. Some studies have been carried out for the reduction of TiO, in oxygen vacancy sites obtained by high-temperature annealing in ultrahigh vacuum (UHV) [12]. TiO, decomposes at high temperatures and low oxygen pressures or at elevated temperatures in the presence of reducing gases, thereby forming suboxides TiO_x with x < 2. Molecular oxygen is typically used by UHV researchers to restore the stoichiometry of ionsputtered or vacuum-reduced TiO, surfaces.

This study aims to further examine the partial reduction of TiO₂ by

hydrogen plasma treatment and to investigate the oxygen adsorption property of partially reduced.

Experimental

Figure 1 illustrates the experimental set-up for the partial reduction of TiO_2 and the oxygen adsorption. The plasma reactor was made of a quartz tube set in an electric furnace. A sample of anatase TiO_2 (JA-1, 0.18µm, Tayca) particles was set in the quartz boat and placed inside the plasma reactor. RF discharge plasma (13.56 MHz) was used to generate glow plasma discharge between copper electrodes attached to the outer surface of the quartz tube. The distance between the electrodes was defined as the electrode gap (50 mm). The reactor temperature, which



*Corresponding author: JinWon Park, Department of Chemical and Biomolecular Engineering, University of Yonsei, 262 Seongsanno, Seodaemungu, Seoul 120-749, Korea, Tel: +82-2-364-1807; Fax: +82-2-312-6401; E-mail: chaeguy@yonsei.ac.kr

Received April 22, 2011; Accepted June 15, 2011; Published June 27, 2011

Citation: Chae Y, Mori S, Suzuki M, Park J (2011) Investigation of Oxygen Adsorption Property of Partially Reduced Tio₂ (Tio₂-X). J Chem Eng Process Technol 2:111. doi:10.4172/2157-7048.1000111

Copyright: © 2011 Chae Y, et al. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

was monitored by thermocouples attached to the inside of the furnace, was changed by controlling the electric power of the furnace.

Table 1 shows the experimental conditions for the partial reduction of TiO2. All experiments of this set were repeated twice to assess reproducibility. Heating temperature was an experimental variable in this experiment. The flow rate, treatment time, and reactor pressure were optimized through repeat experiments. The oxygen adsorption rate and the H₂O formation rate were derived from experimental results. On the first part of the experiment (section 3.1), pretreatment was carried out with argon (flow rate : 40 sccm) and a heating temperature of 500°C for 30 min. This was carried out in order to remove H₂O absorbed on the TiO₂ surface and to quantify the amount of H₂O formed. On the second part of the experiment (section 3.2), reduction was carried out introducing argon and hydrogen (flow rate: 20 sccm, respectively) into the reactor with a fixed pressure at 300 Pa. The RF discharge power delivered to the plasma was 90 W. The heating temperature ranged between 500°C to 1000°C for 40 min. The flow rates of Ar and H₂ were controlled with a mass flow controller (Model 3660, KOFLOC). The reactor pressure was measured at the upstream and downstream points of the reactor using pressure gauges, and the average pressure value was defined as the system pressure. In these experiments, the amount of H₂O produced and the formation rate of H₂O was measured. Water produced by reduction was trapped by a liquid-nitrogen cold trap set downstream of the reactor. The accumulated H₂O was measured every 40 min, and the average H₂O formation rate over a 40-min period was calculated.

After the reduction treatment, it was performed to investigate the oxygen adsorption property of partially reduced TiO_2 . After evacuating the reactor with a rotary pump, dry-air (0.1-atm) gas was introduced in a batch type reactor and the oxygen adsorption was carried out at room temperature. The oxygen was adsorbed on the oxygen vacancy site of TiO_2 formed by reduction. The oxygen adsorbed was measured using a gas chromatograph (GC-8A, SHIMADZU, Japan). The presence of TiO_2 and other titanium oxides (e.g., Ti_2O_3) were observed with X-ray diffraction (XRD) and their intensities were analyzed quantitatively.

Results and Discussion

Partial reduction of TiO, by hydrogen plasma treatment

Hydrogen (H₂) can be dissociated to produce monatomic hydrogen and ionized species using a number of technologies. Monatomic and ionized species of hydrogen, as reducing agents, can be used for the reduction of metals [13,14]. The TiO₂ reduction mechanism investigated in this experiment presumes that monatomic hydrogen (H), ionized species (H₂⁺, H⁺) and electrons (e⁻) produced by the hydrogen plasma treatment has an influence on the reduction of TiO₂. Partially reduced TiO₂ (TiO_{2-x}) and H₂O were produced by reacting diatomic hydrogen (H₂) and monatomic oxygen (O) from TiO₂. The H₂O formation rate was calculated from H₂O produced by reduction and the TiO₂ reduction rate was calculated by measuring the H₂O

Heating temp. (°C)	500 ~ 1000
TiO ₂ sample (g)	0.8
Ar : H ₂ gas(sccm)	20 : 20
Treatment time (min)	40
Reactor pressure (Pa)	300
Plasma input power (W)	90

Table 1: Experimental conditions for the partial reduction of TiO₂.



Figure 2: A plot of the H_2O formation rate as a function of the reaction time used to determine the initial H_2O formation rate. Open circles represent the initial H_2O formation rate. At reaction time zero, the initial H_2O formation rate was estimated by a first-order rate equation, $R=R_0 \exp(-kt)$.



formation rate trapped by liquid-nitrogen. The reaction equation of the partially reduced TiO, is as follows:

$$\text{TiO}_2 + \chi H_2 \rightarrow \text{TiO}_{2x} + \chi H_2 O \tag{1}$$

Figure 2 shows a plot of H_2O formation rate as a function of the reaction time which was used to determine the initial H_2O formation rate. This was estimated by varying the heating temperature from 500°C to 900°C. The H_2O formation was measured until no more H_2O was produced and it took approximately 40 min. At zero reaction time, the initial H_2O formation rate was estimated by a plot following the first-order rate equation. It is given as:

$$R = R_o \exp(-kt) \tag{2}$$

where R is the H_2O formation rate (µmol min⁻¹), R_0 is the initial H_2O formation rate (µmol min⁻¹), t is the time (min), k is the rate constant (min⁻¹). R_0 can be determined by least-squares regression analysis of R versus t.

Figure 3 shows the rutile mole ratio of partially reduced TiO_2 as a function of the heating temperature between 500°C and 1000°C. At 800°C, the rutile mole ratio for plasma-heat treatment was higher than that for heat treatment. Phase transformation anatase to rutile was observed at 800°C for plasma-heat treatment and it was observed at 900°C for heat treatment. It has been reported that phase transformation anatase to rutile occurs at temperatures greater than 600°C [15]. This suggests that the effect of plasma treatment on the

Page 3 of 4

phase transformation is due to a mere temperature increase by heat generation of thermal reaction in plasma discharge

Figure 4 shows the H₂O formation rate as a function of the heating temperature between 500°C and 1000°C. This figure shows that the H₂O formation rate by plasma-heat treatment at 500°C was almost equal to that by heat treatment at 1000°C. In Figure 3, the rutile peak for heat treatment was observed at 1000°C while, no peak was observed at 500°C for plasma-heat treatment. From results of Figures 3 and 4, it is indicated that the plasma-heat treatment has almost the same as the H₂O formation rate comparing that of heat treatment at lower temperature (500°C) and, it has no rutile peak. These results suggest that the plasma-heat treatment at low temperature is almost equal to that by heat treatment at high temperature due to plasma effects such as ionized species (H_2^+, H^+) and electrons (e⁻). This indicates that the increase of H₂O formed by the plasma-heat treatment was not only caused by thermal effects but also caused by plasma effects. In addition, the TiO₂ sample by heat treatment and plasma-heat treatment respectively revealed the color change of surface layer. Figure 5 shows the photograph of partially reduced TiO₂ sample by heat treatment and plasma-heat treatment. The TiO, sample by plasma-heat treatment revealed a dark navy surface layer after about 10 min of exposure to the plasma and the TiO, layer below the dark navy surface layer revealed a discoloration of gray to white. The TiO₂ sample by heat treatment revealed only a gray layer. The dark navy surface layer was observed only in TiO₂ samples treated by plasma. It is reported that the color of TiO, treated by H, plasma was changed white to navy blue due to oxygen vacancy [20]. This indicates that the color of TiO, layer by H, plasma treatment showed dark navy due to oxygen vacancy.

Oxygen adsorption properties of partially reduced TiO,

Some recent research related to an isolated O vacancy has been dealt with the adsorption properties of oxygen [17,18]. The oxygen removal corresponds to a reduction of the surface. The oxygen adsorption is the reverse to the formation of defects on the TiO_2 surface. For defective TiO_2 , a vacancy is created by removal of one bridging oxygen atom. Bridging oxygen atoms are more easily removed than other surface atoms because they are outward the surface plane and the least coordinated ones. Hence, Ti^{4+} surface atoms near the vacancy are formally reduced into Ti^{3+} (sixfold coordinated Ti_6 on the perfect surface becoming fivefold coordinated Ti_{5v} on the defective one). In this section, we investigate the oxygen adsorption property of partially reduced TiO_2 by hydrogen plasma treatment. This is carried out with









plasma input power of 90 W at 600, 700, and 800° C and is repeated twice to assess reproducibility.

Figure 6 shows the ratio of the oxygen adsorption rate to the H_2O formation rate as a function of the adsorption time. As shown in Figure 6, an irregular pattern is observed during the initial oxygen adsorption which become stable as the adsorption time goes by. This result shows that oxygen adsorption to H₂O formation occurs more effectively at lower temperature. Table 2 shows the result data of the H₂O formation amount and the O₂ adsorption amount generated by plasma treatment at 600, 700, and 800°C. As can be seen in Table 2, with increase of the heating temperature increases, the amount of H₂O formation also increases and the amount of oxygen adsorption decreases. The amount of oxygen adsorption was small comparing with the amount of H₂O formed. It is due to the decrease of the specific surface by the increase of heating temperature. From results of Figure 6 and Table 2, it is indicated that the amount of oxygen adsorption is not proportional to the amount of H₂O formed by reduction and is dependent on the heating temperature

Figure 7 shows a plot of the relationship between the amount of H_2O formation and the Ti_2O_3 intensity. Figure 8 shows (included as supplementary data) X-ray Diffraction pattern of partially reduced TiO_2 by heat treatment and plasma-heat treatment at 700°C. The Ti_2O_3 peak was obtained from XRD analysis of partially reduced TiO_2 by plasma treatment. As shown in Figure 7, the Ti_2O_3 intensity increased with the increase of heating temperature. The Ti_2O_3 intensity was dependent on the heating temperature and was proportional to the amount of H_2O formed by reduction. In this study, the formation of H_2O by reduction implies that the formation of oxygen vacancy takes place in bulk TiO_2 . In general, oxygen vacancy takes place by the lost of O ions that bridges Ti ions coordinated. The general type of surface vacancy of TiO_2 is formed by missing O ion that bridges two sixfold-coordinated Ti ions.

Temperature (°C)	o600	•600	□700	∎700	∆800	▲800
H_2O formation amount (µmol)	153.2	160.8	203.2	212	232	274.5
O ₂ adsorption amount (µmol)	3.8	4.4	3.6	4	2.6	2.5

Table 2: The H_2O formation amount and the O_2 adsorption amount (Plasma input power is 90 W at 600, 700, and 800°C).



When a bridging O ion is removed by reduction, the two neighboring Ti ions become fivefold coordinated. For this vacancy, the two Ti ions are very poorly connected from each other, which are somewhat similar to the state in bulk Ti_2O_3 [19,20]. This is in accordance with reports that oxygen adsorption requires oxygen vacancy sites [21]. The amount of oxygen adsorption of partially reduced TiO_2 decreased with the increase of Ti_2O_3 intensity. It is indicated that the decrease of the oxygen adsorption amount is due to the formation of Ti_2O_3 . It is deduced that the formation of Ti_2O_3 has an effect on oxygen adsorption because two fivefold-coordinated Ti ions is similar to the state in bulk Ti_2O_3 . Unfortunately, the detail reason has not been clearly understood yet. The relation of Ti_2O_3 and oxygen adsorption is needed more research.

Conclusions

TiO₂ was partially reduced by hydrogen plasma treatment and the partially reduced TiO₂ showed oxygen adsorption property. The color of TiO₂ reduced by H₂ plasma treatment was changed white to dark navy due to oxygen vacancy. Oxygen adsorption of the partially reduced TiO₂ was occurred with oxygen vacancy. As the heating temperature increases, the H₂O formation amount and the Ti₂O₃ intensity increased and the oxygen adsorption amount decreased. From the relationship of H₂ formation and Ti₂O₃ intensity, the oxygen adsorption was dependent on the formation of Ti₂O₃. The reduction mechanism is perhaps not simple because of the relation between H₂O formation and oxygen adsorption. Further research is necessary to elucidate the reduction mechanism of TiO₃.

Acknowledgement

The authors are grateful to 'The 21st Century COE Program (Chemistry Field), Tokyo Institute of Technology'

References

- Kim SS, Lee H, Na BK, Hyung KS (2004) Plasma-assisted reduction of supported metal catalyst using atmospheric dielectric-barrier discharge. Catal Today 89: 193-200.
- Belmonte T, Thiébaut JM, Michel H, Cardoso RP, Maliska A (2002) Reduction of metallic oxides by late Ar–H₂–N₂ postdischarges. II. Applications to iron oxides. J Vac Sci and Technol A 20: 1353.

 Aarthi T, Madras G (2008) Photocatalytic reduction of metals in presence of combustion synthesized nano-TiO₂. Catal Commun 9: 630-634.

Page 4 of 4

- Kase M, Moriya I, Yotsumoto T, Taoda H (2004) Japanese Patent No. 2004-137087.
- 5. Taoda H, Watawabe E, Nonami T, Fukuya M (2002) Japanese Patent No. 3288265.
- Yoong LS, Chong FK, Dutta BK (2009) Development of copper-doped TiO₂ photocatalyst for hydrogen production under visible light. Energy 34: 1652-1661.
- Changlin Yu, Jimmy Yu, Wanqin Z, Kai Y (2010) WO₃ Coupled P-TiO₂ Photocatalysts with Mesoporous Structure. Catalysis Letters 140: 172-183.
- Bozorgtabar M, Rahimipour M, Salehi M (2010) Effect of thermal spray processes on anatase-rutile phase transformation in nano-structured TiO₂ photo-catalyst coatings. Surface Engineering 26: 422-427.
- Lefèvre G, Fédoroff M, Čerović LJ (2008) Particles adhesion onto massive substrates: experimental measurement and deposition processes. Surface Engineering 24: 272-275.
- Moon J, Park JA, Lee SJ, Zyung T, Kim ID (2010) Pd-doped TiO₂ nanofiber networks for gas sensor applications. Sensors and Actuators B: Chemical 149: 301-305.
- Park H, Kim WR, Jeong HT, Lee JJ, Kim HG, et al. (2011) Fabrication of dyesensitized solar cells by transplanting highly ordered TiO₂ nanotube arrays. Solar Energy Materials and Solar Cells 95: 184-189
- Michael AH, William SE, Craig LP, Charles HF (1999) Interaction of Molecular Oxygen with the Vacuum-Annealed TiO₂(110) Surface: Molecular and Dissociative Channels. J Phys Chem B 103: 5328-5337.
- Izumi A, Ueno T, Miyazaki Y, Oizumi H, Nishiyama I (2008) Reduction of oxide layer on various metal surfaces by atomic hydrogen treatment. Thin Solid Films 516: 853-855.
- Belousov VM, Vasylyev MA, Lyashenko LV, Vilkova NY, Nieuwenhuys BE (2003) The low-temperature reduction of Pd-doped transition metal oxide surfaces with hydrogen. Chem Eng J 91: 143-150.
- 15. Diebold U (2003) The surface science of titanium dioxide. Surf Sci Rep 48: 53.
- 16. Chae YK, Mori S, Suzuki M (2009) Visible-light photocatalytic activity of anatase TiO₂ treated with argon plasma. Thin Solid Film 517: 4260-4263
- Ménétrey M, Markovits A, Minot C (2007) Adsorption of chlorine and oxygen atoms on clean and defective rutile–TiO₂ (1 1 0) and MgO (1 0 0) surfaces. J Mol Struct (THEOCHEM) 808: 71-79.
- Bredow T, Pacchioni G (2002) Electronic structure of an isolated oxygen vacancy at the TiO₂(1 1 0) surface. Chem Phys Lett 355: 417-423.
- Göpel W, Rocker G, Freierabend R (1983) Intrinsic defects of TiO₂(110): Interaction with chemisorbed O₂, H₂, CO, and CO₂. Phys Rev B 28: 3427.
- 20. McKAY JM, Henrich VE (1984) Preparation and properties of the $\rm Ti_2O_3(047)$ surface. Surf Sci 137: 463-472
- Uner D, Tapan NA, Özen İ, Üner M (2003) Oxygen adsorption on Pt/TiO₂ catalysts. Appl Catal A Gen 251: 225-234.