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| Title | Oxidation of hydrophobic alcohols using aqueous hydrogen peroxide over amphiphilic silica particles loaded with titanium(IV) oxide as a liquid-liquid phase-boundary catalyst |
| Author(s) | Choi, Kwang-Min; Ikeda, Shigeru; Ishino, Satoru et al. |
| Citation | Applied Catalysis A General, 278(2), 269-274 https://doi.org/10.1016/j.apcata.2004.10.006 |
| Issue Date | 2005-01-10 |
| Doc URL | https://hdl.handle.net/2115/14643 |
| Type | journal article |
| File Information | ACAG2005-278-2.pdf |



Oxidation of hydrophobic alcohols using aqueous hydrogen peroxide over amphiphilic silica particles loaded with titanium(IV) oxide as a liquid-liquid phase-boundary catalyst

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Abstract

Phase-boundary catalysis (PBC), a new concept of a heterogeneous catalytic system for oxidation of various hydrophobic alcohols with aqueous hydrogen peroxide (H₂O₂) has been investigated. A part the external surface of silica (SiO₂) particles loaded with titanium(IV) oxides was modified with hydrophobic alkyl groups to obtain amphiphilic particles, having both hydrophobic and hydrophilic surfaces on each particle. The amphiphilic particles were spontaneously assembled at interfaces between dual phase mixtures of aqueous solutions and water-immiscible organic compounds. Upon addition to a dual phase mixture of aqueous H₂O₂ and toluene-containing hydrophobic alcohols, these particles acted as an efficient catalyst for the reaction to produce corresponding aldehydes and ketones selectively. Notable features of the PBC system are that the oxidation proceeds even without agitation and that only a few percent of titanium species was detected as dissolved species. Productions of aldehydes and

ketones were also observed when titanium loaded SiO₂ without modification with alkyl groups was employed for the reaction. However, a large amount of loaded titanium on the material was leached during the reaction. These results indicate that surface-covered alkyl groups not only bring about effective contact with hydrophobic alcohols in the organic phase but also give stability against leaching, leading to heterogeneous catalytic functions.

Keywords

liquid-phase oxidation, hydrophobic alcohols, asymmetric surface modification, amphiphilic solid catalyst, phase boundary, titanium, leaching

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1. Introduction

Heterogeneous catalytic oxidation of organic compounds such as alkenes and alcohols in liquid phase has attracted much attention as a promising strategy for environmentally benign organic synthesis [1,2]. A wide variety of oxidants can be used for such reactions. Hydrogen peroxide (H_2O_2) is an ideal one because of its high content of active oxygen, availability, nontoxicity, and non-polluting property, *i.e.*, it produces only water as a byproduct [3,4]. However, since H_2O_2 is generally supplied as an aqueous solution, the use of H_2O_2 is often a problem in cases in which substrates are immiscible in water. In such cases, addition of an amphiphilic solvent (co-solvent) and/or vigorous agitation of the reaction mixture to make an emulsion for achieving sufficient interaction of H_2O_2 with both catalyst(s) and substrate(s) are often required.

We have proposed a new concept of a heterogeneous catalytic system for driving a reaction between a water-immiscible organic compound(s) and aqueous reagent(s) using a solid catalyst without a co-solvent or mechanical agitation [5-8]. For this system, we have prepared solid particles that could assemble at the liquid-liquid phase boundary by partial modification of external surfaces with alkylsilyl groups. It was found that titanium oxide-loaded NaY zeolite and silica (SiO_2) particles partially covered with alkylsilyl groups efficiently catalyzed epoxidation of terminal linear alkenes using aqueous H_2O_2 even without agitation. The reaction system is thus named “phase-boundary catalysis (PBC)”.

We previously reported in detail phenomenological aspects of PBC for epoxidation of terminal linear alkenes [5,6], asymmetric surface structures of catalyst particles [7], and local structures of loaded titanium species [8]. Results of these studies lead to predictions to extend PBC to other organic reactions in order to obtain information on availability and limitations and to obtain mechanistic insights. In this paper, we describe the catalytic properties of a titanium oxide-loaded SiO_2 -based phase-boundary

catalyst for oxidation of various hydrophobic alcohols using H_2O_2 . We focus on oxidation of relatively bulky alcohols that are difficult to use for well-known titanium-containing microporous materials such as titanium silicalite, TS-1, and related materials [9-12] because of their limitation of pore size.

2. Experimental

2.1 Materials

A nonporous silica (Degussa Aerosil 200) was supplied from Nippon Aerosil and used as a support. Titanium(IV) ethoxide ($\text{Ti}(\text{OEt})_4$, 95%) and *n*-octadecyltrimethoxysilane (ODMS, 95%) were purchased from GELEST and used without further purification. Aqueous hydrogen peroxide (H_2O_2 , *ca.* 30%) was purchased from Wako Pure Chemical. All other organic reagents were purified by standard procedures before use [13].

2.2 Catalyst preparation

Amphiphilic w/o-Ti/SiO₂ particles were prepared according to a procedure reported previously [8]. Three grams of silica was added to 150 cm³ of 2-propanol solution containing 145 mg of $\text{Ti}(\text{OEt})_4$ under a dry argon atmosphere. After stirring the mixture for 3 h at room temperature, the solid was collected by centrifugation, dried at 383 K for 2 h under vacuum, and calcined at 773 K for 6 h. The resulting powder is labeled w-Ti/SiO₂. To 10 cm³ of toluene containing 1 mmol of ODMS, 0.5 g of w-Ti/SiO₂ thoroughly mixed with water (16.7 wt.%) was added, and the suspension was shaken for 2 min at room temperature. After the addition of triethylamine (1 mmol),

the suspension was further shaken for 10 min at room temperature. Then the solid was collected by centrifugation, washed twice with 10 cm³ of ethanol, and dried at 383 K for 2 h under vacuum. The thus-obtained white powder is labeled w/o-Ti/SiO₂. By colorimetric analysis of the samples using 1,2-dihydroxy-3,5-benzenedisulfonic acid disodium salt (Tiron), the titanium content was determined to be 158 μmol per 1 g of catalyst.

2.3 Characterization

Thermogravimetry-differential thermal analysis (TG-DTA) was carried out using Bruker 2000A TG-DTA in air (flow rate: 100 cm³ min⁻¹). Typically, ca. 10 mg of a sample was heated in a platinum crucible from room temperature to 1073 K, using heating ramps of 5 K min⁻¹ up to 473 K and 10 K min⁻¹ up to 1073 K. BET surface area was measured at 77 K using a Quantachrome AUTOSORB-1 automated gas sorption system after drying at 423 K for 12 h. Amount of titanium species leached after reaction was determined by using a Perkin-Elmer OPTIMA 3000-XL inductively coupled plasma (ICP) emission spectrometer. The amounts of H₂O₂ before and after the reaction were determined by a standard titration method with 0.02 mol dm⁻³ of aqueous potassium permanganate (KMnO₄, Wako).

2.4 Oxidation of alcohols

Typical procedures for oxidation of alcohols with aqueous H₂O₂ are as follows. To a cylindrical reaction vessel (2 cm in diameter) with a reflux condenser, 8 mmol of alcohol, 67 mg of w/o-Ti/SiO₂ (corresponding to 0.01 mmol of titanium) and 3 cm³ of toluene were successively added. After injection of 1.8 cm³ of aqueous H₂O₂ to the mixture, reactions were performed for 16 h without mechanical agitation. The reaction

temperature was kept at 333 K by the use of a thermostatted oil bath. When necessary, the reaction mixture was stirred with a magnetic stirrer. Amounts of products were determined using Shimadzu GC 2010 and GC-14B gas chromatographs equipped with flame ionization detectors and capillary columns of DB-5 and TC-FFAP, respectively.

3. Results and Discussion

3.1 Structural characteristics of modified particles

Figure 1 shows the TG and DTA curves of w-Ti/SiO₂ and w/o-Ti/SiO₂ samples measured in air in the temperature range of r.t.-1073 K. The TG curve of w-Ti/SiO₂ indicates a slight weight loss below 400 K and no further weight loss up to 1073 K. The weight loss is attributable to dehydration and desorption of water. On the other hand, w/o-Ti/SiO₂ showed an additional large weight loss between ca. 500 K and ca. 773 K in the TG curve. Since the weight loss was accompanied by a major exothermic event starting at ca. 500 K in the DTA curve, it was ascribed to combustion of surface-grafted alkylsilyl groups on the surface of w/o-Ti/SiO₂. Assuming that the remaining powder above 773 K is composed of a mixture of SiO₂ and a small amount of loaded titanium(IV) oxide, the amount of alkylsilyl groups on w/o-Ti/SiO₂ was estimated to be 380 μmol per unit weight of w/o-Ti/SiO₂. From the reported cross section of an octadecylsilyl group (0.226 nm²) [14], ca. 1.4 mmol of alkylsilyl groups can be attached to the surface of w/o-Ti/SiO₂ having a surface area of 200 m². The maximum amount of alkylsilyl groups that can be attached to the w/o-Ti/SiO₂ surface was also estimated using the density of surface hydroxyl groups of the SiO₂ powders used (2.7 hydroxyls nm⁻²) [15]. Assuming that all of the alkylsilyl groups were attached through the reaction with surface hydroxyl, the maximum was estimated to be

ca. 900 μmol per unit weight of w/o-Ti/SiO₂. Although there is a significant difference between these estimations, it is indicated qualitatively that more than half of the surface hydroxyl groups remained on each w/o-Ti/SiO₂ particle. The presence of an appreciable amount of surface hydroxyl groups is also suggested by the weight loss below 400 K due to desorption of H₂O in the TG curve of w/o-Ti/SiO₂ shown in Fig. 1(b). Such low coverage of alkylsilyl groups is thought to be due to the addition of a small amount of water just before grafting of a hydrophobic alkylsilylation agent. Since the hydrophilic w-Ti/SiO₂ particles aggregated by capillary force of water and since the binding water between the particles prevents insertion of the agent into the aggregates, alkylsilyl groups can only be grafted on the outer parts of aggregates. Therefore, the surface of w/o-Ti/SiO₂ was expected to be amphiphilic; one side of the surface of w/o-Ti/SiO₂ was covered with alkylsilyl groups and the remainder retained its original hydrophilic surface. Indeed, through fluorescence microscopy of the modified NaY particles, the remaining surface hydroxyl groups of which were labeled with a fluorescence dye, we have revealed the presence of both hydroxyl and alkylsilyl surfaces on each particle [7].

Upon addition of w-Ti/SiO₂ samples to a dual-phase mixture of toluene and water, w-Ti/SiO₂ was only dispersed in water due to its hydrophilic surface property. On the other hand, in the case of w/o-Ti/SiO₂, most of the particles were assembled at the liquid-liquid phase boundary. As reported previously [5-8,16], this is a phenomenological indication of amphiphilic character, having both hydrophobic and hydrophilic faces, of oxide particles. Based on these results and observations, w/o-Ti/SiO₂ is thought to be assembled at the phase boundary of the water-toluene dual-phase mixture by facing its hydrophobic octadecylsilylated side to the organic phase and its hydrophilic side to the aqueous phase. Further details of amphiphilic characters of particles prepared by the same procedure and their applications will be described elsewhere [17].

3.2 Catalytic activity for oxidation of benzyl alcohol with aqueous H_2O_2

Table 1 summarizes catalytic properties of w-Ti/SiO₂ and w/o-Ti/SiO₂ for oxidation of benzyl alcohol under various conditions. Both w-Ti/SiO₂ and w/o-Ti/SiO₂ particles suspended and agitated in the dual-phase mixture of aqueous H₂O₂ and toluene containing benzyl alcohol gave benzaldehyde with production of other probable by-products, mainly benzoic acid (entries 1 and 2). When these particles were absent, much smaller amounts of products were obtained (entry 3), indicating that the reaction was induced by these catalysts. However, it was noted, especially for w-Ti/SiO₂, that a large amount of loaded titanium was leached from the surface into the aqueous phase, as determined from the results of ICP analysis for the aqueous phase after the reaction. When aqueous H₂O₂ and benzyl alcohol were added to the aqueous phase that was corrected after the reaction of entry 1 and stirring the mixture under the same reaction conditions, an appreciable amount of benzaldehyde was produced (entry 4). Thus, observed liberation of benzaldehyde from the w-Ti/SiO₂ suspension was mainly induced by such leached titanium species. Although the w/o-Ti/SiO₂ suspension gave a ca. 1.5-times larger amount of benzaldehyde than did the w-Ti/SiO₂ suspension and leaching of titanium was suppressed to some extent (entry 2), this may also include the influence of dissolved titanium species. On the other hand, when the reaction was performed under static conditions, i.e., PBC conditions, a relatively large amount of benzaldehyde was produced from the w/o-Ti/SiO₂ suspension (entry 6). In this case, moreover, much less leaching was observed, while the w-Ti/SiO₂ suspension showed the same behavior as that of the above agitation system; reaction by leached titanium might be predominant (entries 5 and 7). The remaining aqueous solution of w/o-Ti/SiO₂ after the reaction under such static conditions did not give a detectable amount of benzaldehyde, as expected (entry 8). In addition, when the amount of

catalyst was decreased to 3.4 mg (corresponding to 0.5 μmol of Ti), the turnover number (TON) of benzaldehyde based on Ti approached ca. 530 (entry 9). These results imply that when the reaction was performed under PBC conditions, modification with alkylsilyl groups brought about sufficient stability of titanium active sites to leaching. Accordingly, it could be confirmed that the PBC using w/o-Ti/SiO₂ was a heterogeneous catalytic system for selective oxidation of benzyl alcohol (see below).

3.3 Catalytic properties for oxidation of various hydrophobic alcohols

In order to examine the availability of the w/o-Ti/SiO₂-based PBC, oxidation of various aromatic and cyclic alkyl alcohols using aqueous H₂O₂ was performed. The results are summarized in Table 2. Primary benzylic alcohols were efficiently converted into corresponding aldehydes, and their reaction rates were slightly dependent on substituents (-Cl, -OCH₃, and -CH₃) and their positions (*p*-, *m*-, and *o*-) (entries 1-6). Similarly, secondary benzylic alcohols were also oxidized to corresponding ketones in relatively high selectivity (entries 7-8). On the other hand, poor selectivities for oxidation of allylic alcohols such as cinnamyl alcohol was obtained (entry 9), owing to the activity of loaded titanium sites for epoxidation [12,18-20]. It was noted that the catalytic system could be utilized for oxidation of secondary cyclic alcohols such as cyclohexanol and cyclooctanol, which are relatively inactive toward oxidation, to corresponding ketones (entries 10-11). Oxidation of a series of aliphatic alcohols has been widely examined using microporous titanosilicalites such as TS-1 [9-11]. However, these bulky alcohols reported here were not employed as substrates in such titanium-based heterogeneous catalysts owing to the limitation of their pore sizes. Hence, although overall rates were not satisfactory, the present PBC system might enable a titanium-based catalyst to be used for oxidation of various bulky alcohols.

3.4 Role of alkylsilyl groups

As previously investigated using Ti K-edge X-ray absorption near-edge fine structure (XANES) analysis [8], the loaded titanium species on w/o-Ti/SiO₂ were mainly those with tetrahedral coordination (T_{tet}) with a small content of octahedrally coordinated ones (T_{oct}). The former was attributable to the isolated titanium and the latter included titanium dimers, oligomers, and/or bulk (TiO₂)-like microclusters [21-24]. The efficiency of H₂O₂ utilized for the reaction measured in some selected samples was estimated to be below 20% (data not shown). This suggests unproductive decomposition (or auto-decomposition) of H₂O₂ on these T_{oct} sites under a large excess of H₂O₂ [8], and thereby the active species might be ascribed to T_{tet}. It has also been clarified in our previous study using ultraviolet and visible-light diffuse reflectance (UV-Vis-DR) spectroscopy in relation to catalytic activity [8] that there are three types of T_{tet} on w/o-Ti/SiO₂. These are T_{tet} anchoring an acidic hydroxyl (T_{tet}(OH)) located on the hydrophilic and hydrophobic surfaces (w-T_{tet}(OH) and o-T_{tet}(OH)) and T_{tet} directly attached to an alkylsilyl group (T_{tet}(OSiR)). The latter was formed via reaction of an acidic hydroxyl of T_{tet}(OH) with an alkylsilane agent on the hydrophobic surface. Schematic structures of these titanium sites are shown in Fig. 2. The results of oxidation of benzyl alcohol summarized in Table 1 suggest that w-T_{tet}(OH) sites probably do not contribute to the heterogeneous catalytic property of w/o-Ti/SiO₂ because these must be present on w-Ti/SiO₂ as sole T_{tet} sites. As described above, T_{tet} sites were not stable under the present reaction conditions, i.e., oxidation proceeded by mainly leached titanium species (Table 1, entries 4 and 7). Thus, two probable species located on the hydrophobic surface of w/o-Ti/SiO₂, o-T_{tet}(OH) and T_{tet}(OSiR), might induce heterogeneous catalytic activity, though it is not clear at present that whether one of them is active or both are active. According to these speculations, surface-grafted alkylsilyl groups were considered to give particles two beneficial effects for the use of a

heterogeneous catalyst. One is to give hydrophobicity of T_{tet} sites inducing effective contact with hydrophobic alcohols, and the other is to prevent leaching by covering with siloxane networks of alkylsilylation agents.

4. Conclusions

It was found that amphiphilic SiO_2 particles loaded with titanium(IV) oxide species acted as a catalyst for the oxidation of benzylic and cyclic alkyl alcohols using aqueous H_2O_2 under static conditions, i.e., phase boundary catalytic conditions. To the best of our knowledge, this is the first example of oxidation of bulky hydrophobic alcohols using aqueous H_2O_2 over a heterogeneous titanium catalyst. Such catalytic functions were probably realized by effective contact of catalyst particles with H_2O_2 and hydrophobic alcohols, respectively, as well as the effect of stabilization of active titanium sites by surface-grafted alkylsilyl groups. The results should provide useful information for an alternative strategy to design catalytic materials.

Acknowledgements

The authors are grateful to Nippon Aerosil Co., Ltd. for supplying silica samples. This research was partly supported by RITE research grants. Professor K. Kaneda and K. Ebitani (Osaka University) are acknowledged for their stimulating suggestions and discussion.

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Figure Captions

Fig. 1. TG-DTA curves of (a) w-Ti/SiO₂ and (b) w/o-Ti/SiO₂.

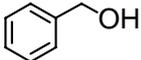
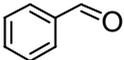
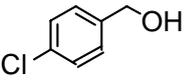
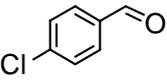
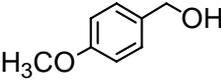
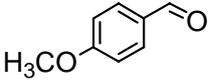
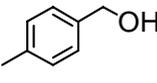
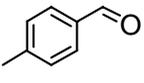
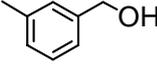
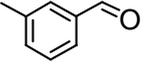
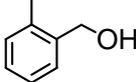
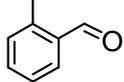
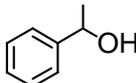
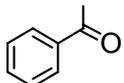
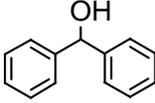
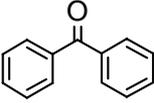
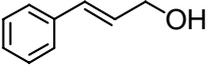
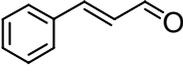
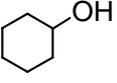
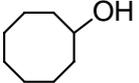
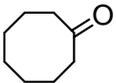
Fig. 2. Schematic illustrations of local structures and distributions of tetrahedral titanium oxide species on a w/o-Ti/SiO₂ sample. (i) T_{tet}(OSiR) sites located on the hydrophobic surface, (ii) T_{tet}(OH) sites located on both hydrophilic and hydrophobic surfaces (w-T_{tet}(OH) and o-T_{tet}(OH), respectively).

Table 1.Oxidation of benzyl alcohol with H₂O₂ in water-toluene dual-phase system^a

| entry | catalyst | condition | aldehyde ^b | select. ^c | leaching ^d | TON |
|-------|---------------------------------------|--------------------|-----------------------|----------------------|-----------------------|-----|
| | | | / mmol | /% | /% | |
| 1 | w-Ti/SiO ₂ | stirr ^e | 0.98 | 89 | 25 | 98 |
| 2 | w/o-Ti/SiO ₂ | stirr ^e | 1.32 | 74 | 15 | 132 |
| 3 | none | stirr ^e | 0.08 | 100 | - | - |
| 4 | soln.-1 ^g | stirr ^e | 0.61 | 85 | - | - |
| 5 | w-Ti/SiO ₂ | stat ^f | 0.80 | 96 | 25 | 80 |
| 6 | w/o-Ti/ SiO ₂ | stat ^f | 1.29 | 97 | 2 | 129 |
| 7 | soln.-2 ^h | stirr ^e | 0.61 | 85 | - | - |
| 8 | soln.-3 ⁱ | stirr ^e | 0 ^k | - | - | - |
| 9 | w/o-Ti/ SiO ₂ ^j | stat ^f | 0.26 | 100 | 0 ^k | 530 |

^aAll reactions were carried out at 333 K for 16 h with benzyl alcohol (8 mmol), toluene (3 cm³), 30 % H₂O₂ (1.8 cm³), and catalyst (67 mg). ^bBenzaldehyde. ^cSelectivity for benzaldehyde production defined as the percentage of the aldehyde yield to the total amount of detected products. The percentage of titanium in the solution after the reaction. ^eReaction was carried out with vigorous mechanical agitation. ^fReaction was carried out without agitation. ^gThe aqueous phase of entry 1 after the reaction was used. ^hThe aqueous phase of entry 5 after the reaction was used. ⁱThe aqueous phase of entry 6 after the reaction was used. ^j3.4 mg of catalyst was used. ^kNot detected (< 10⁻³ μmol).

Table 2.Oxidation of various alcohols catalyzed by w/o-Ti-SiO₂ using H₂O₂ as an oxidant^a

| entry | substrate | product | yield (mmol) ^b | select. ^c (%) |
|-------|---|---|---------------------------|--------------------------|
| 1 |  |  | 1.29 | 97 |
| 2 |  |  | 1.33 | 92 |
| 3 |  |  | 1.20 | 74 |
| 4 |  |  | 1.81 | 80 |
| 5 |  |  | 1.48 | 92 |
| 6 |  |  | 1.15 | 99 |
| 7 |  |  | 0.85 | 100 |
| 8 |  |  | 0.91 | 100 |
| 9 |  |  | 0.64 | 35 |
| 10 |  |  | 0.50 | 100 |
| 11 |  |  | 1.11 | 88 |

^aAll reactions were carried out at 333 K for 16 h with alcohol (8 mmol), toluene (3 cm³), 30 % H₂O₂ (1.8 cm³), and catalyst (67 mg). ^bYield of the produced aldehyde determined by GC using internal standard technique. ^cSelectivity for aldehyde production defined as the percentage of the aldehyde yield to the total amount of products.

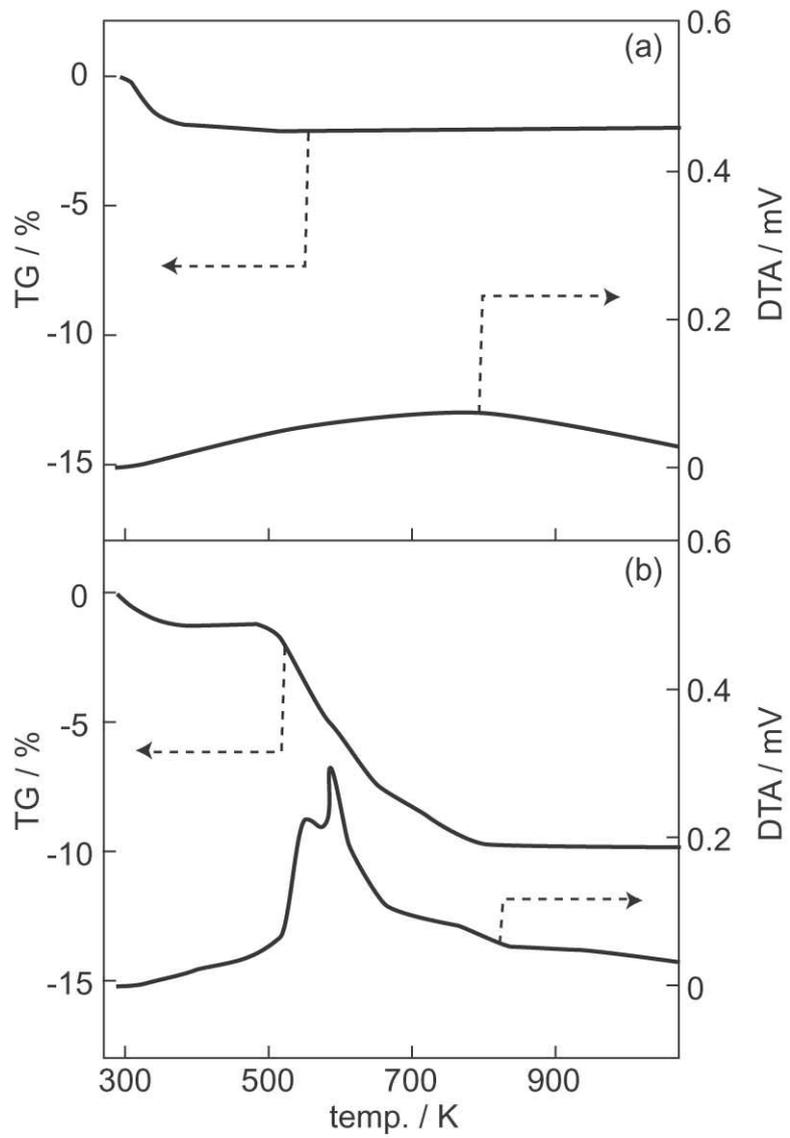


Fig. 1. K.-m. Choi et al.

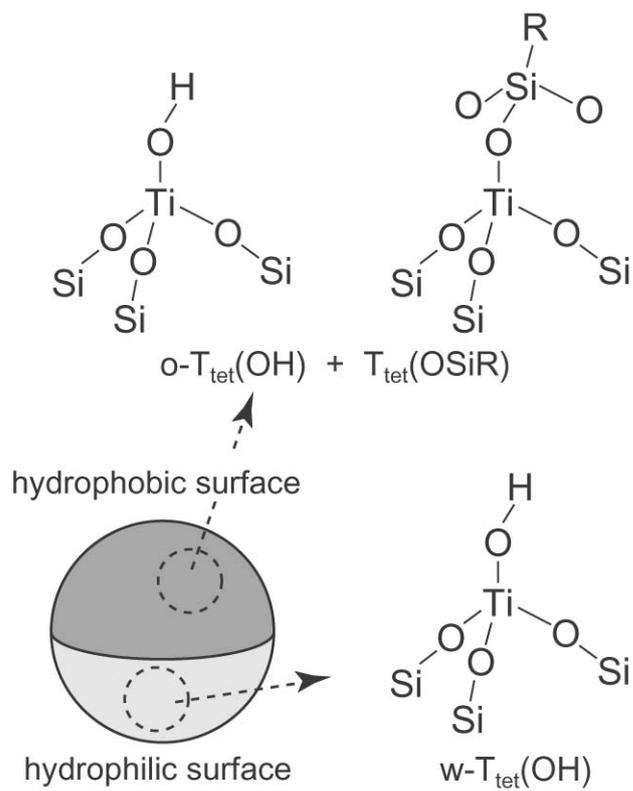


Fig. 2. K.-m. Choi et al.