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Applied Catalysis A: General 278 (2005) 269–274

APPLIED CATALYSIS A: GENERAL

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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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Received 26 May 2004; received in revised form 24 September 2004; accepted 6 October 2004

Abstract

Phase-boundary catalysis (PBC), a new concept of a heterogeneous catalytic system for oxidation of various hydrophobic alcohols with aqueous hydrogen peroxide (H_2O_2), has been investigated. A part the external surface of silica (SiO_2) 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 H_2O_2 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 SiO_2 without modification with alkyl groups was employed for the reaction. However, a large amount of titanium loaded 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.
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Keywords: Liquid-phase oxidation; Hydrophobic alcohols; Asymmetric surface modification; Amphiphilic solid catalyst; Phase-boundary; Titanium; Leaching

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, non-toxicity, 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-

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doi:10.1016/j.apcata.2004.10.006

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 attempts 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 limitations of pore size.

2. Experimental

2.1. Materials

A non-porous silica (Degussa Aerosil 200) was supplied from Nippon Aerosil and was used as a support. Titanium(IV) ethoxide ($Ti(OEt)_4$, 95%) and *n*-octadecyltrimethoxysilane (ODMS, 95%) were purchased from GELEST and were 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 SiO_2 particles loaded with titanium(IV) oxide particles were prepared according to a procedure reported previously [8]. Three grams of SiO_2 was added to 150 cm^3 of 2-propanol solution containing 145 mg of $Ti(OEt)_4$ under a dry argon atmosphere. After the mixture was stirred 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/SiO_2. To 10 cm^3 of toluene containing 1 mmol of ODMS, 0.5 g of w-Ti/SiO_2 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 cm^3 of ethanol, and dried at 383 K for 2 h under vacuum. The thus-obtained white powder is labeled w/o-Ti/SiO_2. 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 a Bruker 2000A TG-DTA instrument in air (flow rate: 100 $cm^3\ min^{-1}$). 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. The 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 H_2O_2 before and after the reaction were determined by a standard titration method with 0.02 mol dm^{-3} of aqueous potassium permanganate ($KMnO_4$, Wako).

2.4. Oxidation of alcohols

Typical procedures for oxidation of alcohols with aqueous H_2O_2 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/SiO_2 (corresponding to 0.01 mmol of titanium) and 3 cm^3 of toluene were successively added. After injection of 1.8 cm^3 of aqueous H_2O_2 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

Fig. 1 shows the TG and DTA curves of w-Ti/SiO_2 and w/o-Ti/SiO_2 samples measured in air in the temperature range of RT−1073 K. The TG curve of w-Ti/SiO_2 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/SiO_2 showed an additional large weight loss between ca. 500 and 773 K in the TG curve. Since this 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 w/o-Ti/SiO_2. Assuming that the remaining powder above 773 K is composed of a mixture of SiO_2 and a small amount of loaded titanium(IV) oxide,

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