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Biphasic epoxidation of 1-octene with H_2O_2 catalyzed by amphiphilic fluorinated Ti-loaded zirconia

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Abstract

A series of amphiphilic fluorinated zirconia containing titanium was prepared by titanium impregnation followed by fluorination and alkylsilylation of zirconium oxide. Physical properties of the resulting samples were characterized by XRD analysis, UV–vis spectroscopy, BET surface area analysis and EDAX analysis. The effects of fluorine and alkylsilane groups on the samples were studied by the epoxidation of 1-octene with aqueous hydrogen peroxide. The epoxidation of alkenes is one of the most important methods of functionalizing simple hydrocarbons. The amphiphilic fluorinated catalysts were more active and more efficient than the conventional titania–silica and zirconia–silica mixed oxides in linear alkene epoxidation; enhanced by the presence of alkylsilane and fluorine groups in the catalysts. Modification with alkylsilane successfully induces the hydrophobic behavior of zirconia which is hydrophilic in nature; whereas fluorine was chosen for its electron-withdrawing effect which further activates the titanium active sites.

Keywords: Fluorination; Alkylsilylation; Linear alkene epoxidation; Hydrogen peroxide; Electron-withdrawing effect

1. Introduction

Epoxides are substances of important commercial value and have found use in diverse areas. Currently, one of the most intensively researched areas of chemistry is the search for novel epoxidation methods [1–5]. Despite numerous reports in the literature, the epoxidation of terminal alkenes remains a challenge in petrochemistry. To date, liquid-phase epoxidation with hydrogen peroxide catalyzed by transition metals has been largely dominated by the use of complexes in solution [6]. However, while these homogeneous systems may be suitable for the preparation of fine chemicals or pharmaceuticals, the obvious problem of the catalyst separation and recovery has so far hampered their use in larger scale operations. In most cases, separation difficulties have been the key barrier for commercialization of delicate synthetic chemical methodologies. For this reason, the heterogeneous catalytic system offers a better alternative nowadays since it is safer, possesses higher efficiency and environmentally acceptable, eventually reducing plant maintenance and minimizes environmental harms.

Recently, we have reported a new heterogeneous system to enhance the epoxidation catalytic activity by means of fluorination and alkylsilylation of a titanium-containing catalyst [7]. The concept is based on the idea that fluorine is highly electronegative which possesses strong affinity and tendency to attract electrons from its surrounding. This is called as ‘electron-withdrawing’ effect [8,9]. Fluorine is able to attract electrons from elements nearby and thus strengthens the bond between these two elements. With this characteristic, fluorine is expected to further activate an active site by making the active site more electrophilic, easier to be attacked by nucleophile substrates like alkenes. On the other hand, alkylsilylation is aimed to induce hydrophobicity of catalyst which is a prerequisite in any epoxidation using hydrogen peroxide as oxidant [10–12]. Hence, the objective of this paper is to carefully investigate the effect of various catalyst modification conditions, such as amphiphilicity, different alkylsilane groups and effect of stirring, on the catalytic epoxidation of 1-octene. By deepening the understanding on the effects of various

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experimental parameters, an optimized system for an efficient epoxidation reaction could be designed.

2. Results and discussion

2.1. Physical properties of catalysts

Fig. 1 shows the apparent distribution of the series of modified Ti–ZrO_2 catalysts suspended in H_2O_2 and 1-octene mixture. Only the unmodified Ti–ZrO_2 with naturally hydrophilic behavior was dispersed in the aqueous phase. This suggests that hydrophobicity is introduced to the particles upon fluorination and alkylsilylation [14]. A small amount of water was added to the dried Ti–ZrO_2 powder before mixing with alkylsilane to adjust the surface coverage of alkylsilyl groups on the particle surface. The particles were aggregated by the capillary force of water resulting in alkylsilane groups can only react with the outer surface of the aggregates. Therefore, the particles surface is amphiphilic, having both the hydrophilic and hydrophobic faces.

Fig. 2 shows the XRD patterns which demonstrate the effect of different fluorine concentration onto the zirconia structure as the support material. All samples demonstrate monoclinic phase of ZrO_2 and this crystalline structure remains unaltered upon fluorination. Unlike the widely used zeolite-based support materials which succumb to fluorination, zirconia is highly stable to modification.

Monoclinic ZrO_2 has surface area ~30 m^2/g. The surface area of Ti–ZrO_2 (31 m^2/g), w/o-OTS-Ti–ZrO_2 (29 m^2/g), F-Ti–ZrO_2 (28 m^2/g), w/o-OTS-F-Ti–ZrO_2 (28 m^2/g) and w/o-CTMS-F-Ti–ZrO_2 (24 m^2/g) indicating the effect of fluorination and alkylsilylation on the surface of the catalysts is negligible. The amounts of alkylsilane and fluorine groups, measured by EDAX, that were attached on the zirconia surface are relatively small. Therefore, the surface area of zirconia is not much altered. The presence of alkylsilane and fluorine components in the samples is proven in the EDAX result. The semi-quantitative EDAX analysis indicates the amounts of silicon and fluorine is ca. 2.0% and 1.2%, respectively. The local environments of titanium species which appear to be the active sites for the epoxidation reaction have been seriously investigated by UV–vis diffuse reflectance in our previous report [7]. Fluorination of the sample was found to induce transformation of some octahedral titanium framework to the tetrahedral structure resulting in a considerable enhancement in the epoxidation reaction. It is generally accepted that isolated Ti(IV) in tetrahedral form are considered the most active species in epoxidation reaction [15,16].

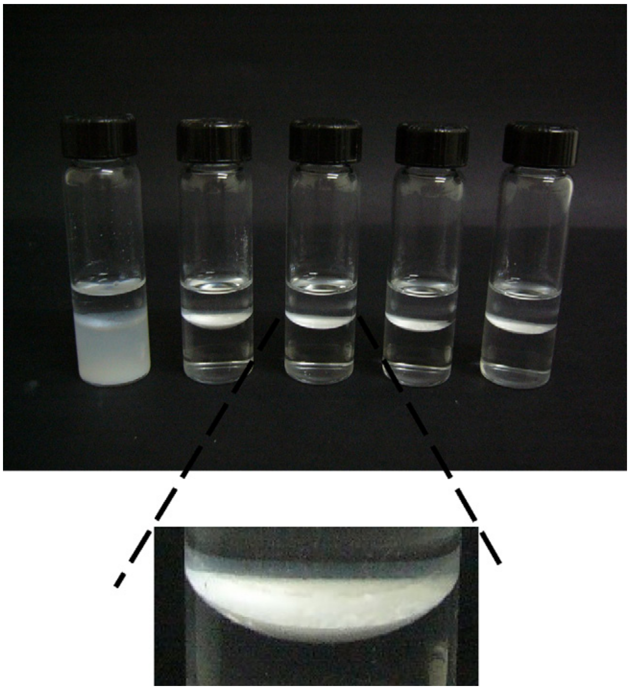

Fig. 1. The photographs showing the distribution of Ti-ZrO_2, w/o-OTS-Ti–ZrO_2, F-Ti–ZrO_2, w/o-OTS-F-Ti–ZrO_2 and w/o-CTMS-F-Ti–ZrO_2 (from left to right) in the mixture of 1-octene–H_2O_2.

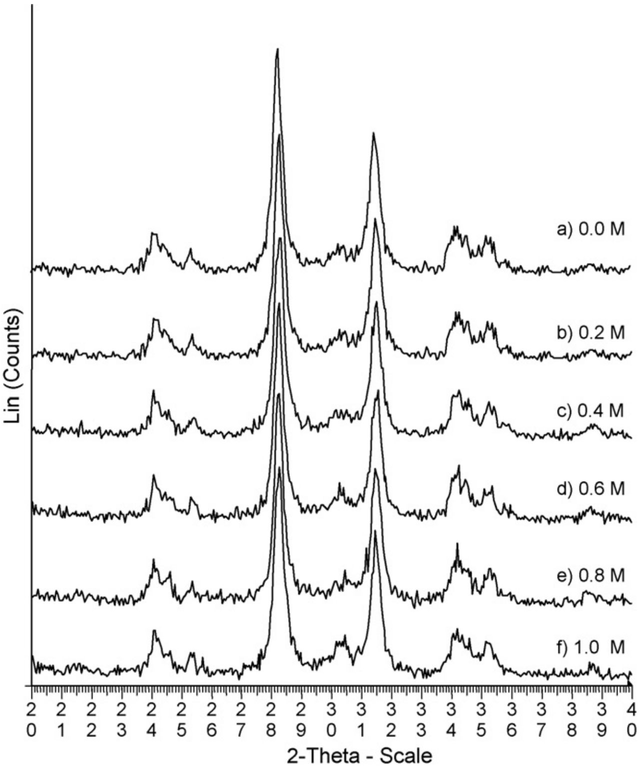

Fig. 2. X-ray diffractograms to demonstrate the effect of different fluorine concentrations on the Ti–ZrO_2 structure.

2.2. Catalytic epoxidation

2.2.1. Effects of alkylsilylation and fluorination

Fig. 3 demonstrates the kinetic curves of the epoxidation of 1-octene with aqueous H_2O_2 in the presence of modified Ti-ZrO_2 catalysts. Generally, modification by alkylsilane (OTS and CTMS) and fluorosilicate led to a considerable yield enhancement. In particular, the partially alkylsilylated catalysts (w/o-OTS-, w/o-OTS-F-, w/o-CTMS-F-) showed higher activities than the hydrophilic Ti–ZrO_2. OTS and CTMS are effective hydrophobic-inducing agents. By the partial modification with our method, the catalysts possess

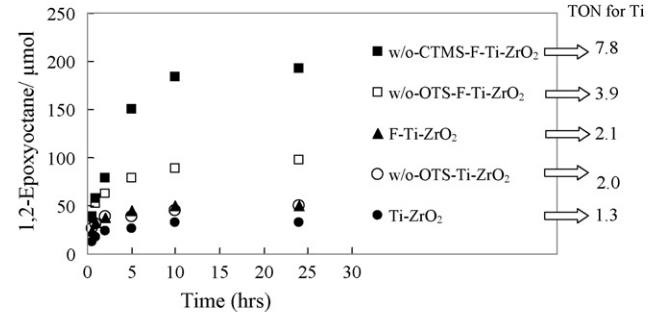

Fig. 3. Kinetic curves of the epoxidation of 1-octene with aqueous H_2O_2 in the presence of modified Ti–ZrO_2 catalysts at room temperature for 24 h.

amphiphilic behavior, containing both hydrophilic and hydrophobic regions. As a result, titanium active sites on the catalysts were exposed to both organic octene substrate and aqueous H_2O_2. The continuous supply of H_2O_2 and 1-octene to the active sites promises a higher yield. On the other hand, the positive effect of fluorination is apparent. The highly electronegative fluorine would withdraw the electrons from Ti towards the direction where the fluorine is located ($Ti^{4+} \rightarrow F^-$). This results in an electrophilic Ti species which is more vulnerable to the attack by π-electron clouds of the nucleophilic alkene.

2.2.2. *Effect of various alkylsilane groups*

Fig. 4a compares the effectiveness of OTS and CTMS alkylsilane in the epoxidation reaction. Hydrophobic-inducing alkylsilane groups have the function to attract organic substrates towards the active sites on the catalyst. However, their molecular structures have an impact on the reaction. OTS consists of 18-carbon chain whereas CTMS comprises of three methyl groups. Hence, OTS which is a bulky molecule has a steric constrain effect on the organic substrate uptake. Organic substrates are relatively more difficult to approach the active sites on the catalyst surface due to the physical barrier formed from the larger OTS molecules. Comparatively, 1-octene reached Ti active sites in a higher frequency when CTMS was used as the alkylsilane source resulting in a higher yield of product.

2.2.3. *Effect of partial and fully alkylsilylation*

Surface coverage of alkylsilane groups on catalyst imposes effects on the epoxidation reaction. Fig. 4b exhibits the epoxide yield obtained from the partially alkylsilylated (w/o-OTS-F-Ti–ZrO_2) and fully alkylsilylated catalyst (o-CTMS-F-Ti–ZrO_2). In the preparation of partially alkylsilylated catalyst, a small amount of water was added in order to prompt the aggregation between catalyst particles. The aggregation of particles allowed only the outer surface to be alkylsilylated, whereas the inner surface remained hydrophilic. The drying process after the alkylsilylation broke the aggregation generated the particles with both hydrophobic and hydrophilic surface. On the other hand, surface of the fully alkylsilylated catalyst was totally covered by hydrophobic alkylsilane, which prevent the aqueous substrates from diffusing into the titanium sites. Therefore, partial alkylsilylation is favored since it enabled a continuous supply of both organic and aqueous substrates to reach the active sites.

2.2.4. *Effect of stirring*

The objective of stirring in one reaction is mainly to increase the contact frequency and mass transfer between the substrates and the catalysts. Since the continuous supply of substrates to catalyst is feasible by having the amphiphilicity on the surface of support materials in this reaction, the necessity for stirring to enhance the product yield is greatly reduced. As shown in Fig. 5, the activity of hydrophilic Ti–ZrO_2 was only appreciable under the condition of vigorous stirring. However, fluorinated catalysts gave the yield even under static condition and the product yield was increased when the reaction was carried out with stirring. As can be seen in Fig. 1, beside electron-withdrawing effect, fluorination induced certain degree of hydrophobicity to the sample resulted in the fluorinated catalysts were remained at the interphase of H_2O_2 and 1-octene. This provides a better chance of contact between aqueous and organic substrates. However, F-Ti–ZrO_2 dropped into the aqueous phase by gravity after a few hours staying at the phase boundary. This suggesting a more effective hydrophobic-inducing agent, such as alkylsilane, is preferred for introducing hydrophobicity.

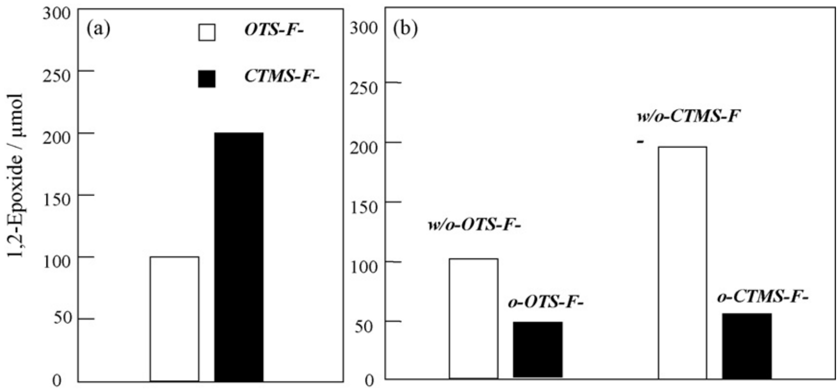

Fig. 4. (a) Effect of various alkylsilane attachment and (b) effect of partially or fully alkylsilylation on the epoxidation of 1-octene.

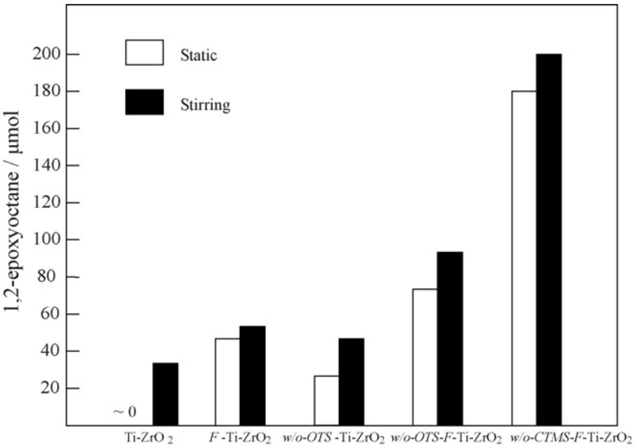

Fig. 5. Effect of stirring on the epoxidation of 1-octene by various modified Ti–ZrO_2 at room temperature for 20 h.

On the other hand, the activity of partial alkylsilylated catalysts (w/o-OTS-, w/o-OTS-F-, w/o-CTMS-F-) was relatively independent of the stirring factor. This is one of the most prominent characteristics of amphiphilic catalysts, which enables a continuous supply of H_2O_2 and organic substrates to the active sites on the particles under static condition.

In order to check the possibility of leaching of Ti species during epoxidation, an experiment performed under similar reaction condition was interrupted after 30 min. The H_2O_2 and 1-octene mediums were removed with a syringe and immediately transferred to another glass tube under the same condition. The compositions were then monitored for 24 h. No activity was found after the catalysts were removed from the reaction, suggesting that no active Ti species had leached out from the catalyst. Therefore, the activity is only attributed to the Ti atoms incorporated onto the surface of the support material.

From the above-synthesized samples, w/o-CTMS-F-Ti–ZrO_2 appeared to be the most efficient catalyst for epoxidation of 1-octene with H_2O_2. The excellent catalytic activity of this catalyst was attributable to the electron-withdrawing effect introduced by fluorination and amphiphilicity introduced by partial alkylsilylation of CTMS. Fluorination resulted in electrophilic Ti active sites which were attacked easily by nucleophilic alkene while amphiphilicity offered an enhancement in substrate transfer between the immiscible liquid–liquid phases. With these characteristics, this catalyst was well performed under static condition in the epoxidation reaction at room temperature.

3. Conclusion

In conclusion, fluorinated Ti–ZrO_2 particles having both hydrophilic and hydrophobic surfaces were prepared by fluorination and partial alkylsilylation. The combination of fluorination and alkylsilylation of Ti–ZrO_2 were successfully gave a synergy effect on the heterogeneously epoxidation of 1-octene by aqueous H_2O_2 under optimized experimental condition.

4. Experimental

4.1. Catalyst preparation

Zirconium(IV) hydroxide [$Zr(OH)_4$] was used as obtained. First, tetrapropyl orthotitanate [$Ti(OPr)_4$] was impregnated from cyclohexanol solution into zirconium hydroxide by vigorous stirring at 343 K until cyclohexanol was dried [13]. The molar amount of Ti was 500 μmol g^{-1} of zirconium hydroxide. The resulting dried sample was calcined at 873 K for 2 h to produce Ti–ZrO_2.

Ammonium hexafluorosilicate [$(NH_4)_2SiF_6$] was used as the source of fluorination. A series of ammonium hexafluorosilicate solution with different concentrations were prepared: 0.2 M, 0.4 M, 0.6 M, 0.8 M and 1.0 M. One grams of the Ti–ZrO_2 prepared above was immersed in 10 cm^3 of each solution and was shaken for 15 min at room temperature. The particles were then collected through centrifugation and dried at 383 K. This sample was labeled as F-Ti-ZrO_2. The F-Ti–ZrO_2 was then further modified by alkylsilylation.

For the alkylsilylation, two alkylsilane were used. They were octadecyltrichlorosilane (OTS) and chlorotrimethylsilane (CTMS). First, a small amount of water (~50%, w/w) was added to the F-Ti–ZrO_2 to lead the aggregation among powder particles. Then, the wetted F-Ti–ZrO_2 was suspended in 10 cm^3 toluene containing 500 μmol of OTS or CTMS. The suspension was centrifuged in order to remove excessive unreacted alkylsilane and washed with toluene and ethanol. The resulting amphiphilic samples were then dried at 383 K overnight. The partially alkylsilylated particles obtained were labeled as w/o-OTS-F-Ti–ZrO_2 and w/o-CTMS-F-Ti–ZrO_2. Alkylsilylation of Ti–ZrO_2 sample without fluorination was prepared as well to give w/o-OTS-Ti–ZrO_2. The label 'w/o-', refers to water phase/organic phase, is to indicate the samples' amphiphilicity.

As a reference, fully alkylsilylated hydrophobic F-Ti–ZrO_2 particles whose external surfaces were thoroughly covered with alkylsilane were also prepared without mixing water in the first step of the above described procedure for preparation of amphiphilic fluorinated catalyst; they are called o-OTS-F-Ti–ZrO_2 and o-CTMS-F-Ti–ZrO_2. Here, the label 'o-', refers to organic phase, is to indicate the samples' hydrophobicity.

4.2. Characterizations and catalytic test

The samples were characterized by X-ray diffraction (XRD) on a Bruker D8 Advance instrument using Cu Kα radiation with 40 kV, 40 mA and $\lambda = 1.5418$ Å. Fluorine element in the catalysts was semi-quantitatively measured with EDAX Philips XL 40 instrument at 20 kV. Thermo Finnigan Qsurf Series BET surface area analyzer was used to analyze surface area of the catalysts.

In a typical epoxidation reaction, 50 mg of catalyst powders were placed in a glass tube with 4 ml of 1-octene (Aldrich) and 1 ml of 30% aqueous H_2O_2 (Hanns). The reaction was performed with stirring or without stirring at ambient temperature for 24 h. The resulting product was withdrawn and analyzed at certain interval with gas chromatograph (GC). Gas chromatograph–mass spectrometer (GC–MS) was used to verify the product.

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