

Hydrophobic fluorinated TiO₂–ZrO₂ as catalyst in epoxidation of 1-octene with aqueous hydrogen peroxide

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Abstract

A new heterogeneous oxidation catalyst was prepared by impregnation of TiO₂ from titanium(IV)tetra-2-propoxide on the surface of ZrO₂. The surfaces of TiO₂–ZrO₂ particles were then modified by the fluorination of ammonium hexafluorosilicate and followed by alkylsilylation of *n*-octadecyltrichlorosilane (OTS). The resulting catalysts were characterized by X-ray diffraction (XRD), nitrogen adsorption isotherm, UV–Vis Diffuse Reflectance (UV–Vis DR), and Energy Dispersive X-Ray Analysis (EDAX) techniques. The catalytic potential of catalysts for oxidation reactions has been verified in the liquid phase epoxidation of 1-octene to 1,2-epoxyoctane with aqueous hydrogen peroxide. It is demonstrated that the fluorination and alkylsilylation enhance the catalytic activity of TiO₂–ZrO₂. A high catalytic activity of the modified TiO₂–ZrO₂ was related to the modification of the local environment of titanium active site and increasing the hydrophobicity of catalyst particles by fluorination and alkylsilylation.

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1. Introduction

It is generally accepted that heterogeneous catalysis has many advantages compared to the homogeneous system. However, there is the limitation of the application for this system, especially for zeolite. For example, serious drawback has been found for TS-1 due to its restriction to substrate molecules with kinetic diameter <5.5 Å. In TS-1, the active sites for the material are located in the internal framework [1–3] and this limits the application to substrates with relatively small molecular sizes [4]. Large molecules with ring structures are not accessible, reducing its catalytic capabilities. It was explained that the high catalytic activity of TS-1 has a correlation to its intrinsic properties such as the existence of Ti in the framework and its MFI structure [1–3]. These properties certainly give a synergy effect on the catalytic activities of hydrocarbons. Due to the importance of Ti active sites, there is a need to design a system where they can be located at the surface which enables it to freely directly interact with every substrate. Based on this problem, in

this paper, a new catalytic system, hydrophobic fluorinated TiO₂–ZrO₂ is proposed as an oxidation catalyst. The catalyst particles were prepared by deposition of titanium species from titanium(IV)tetra-2-propoxide onto non-porous ZrO₂ and followed by fluorination of ammonium hexafluorosilicate and attachment of octadecylsilyl groups from *n*-octadecyltrichlorosilane (OTS). Here, zirconia is used as the support because this material is resistant to fluorination. By using this new system, it is expected that any kind of substrate can freely interact with catalytic active site which is located on the surface of the catalyst. To examine this catalytic system, the epoxidation of 1-octene by using aqueous H₂O₂ was chosen as a model reaction.

2. Experimental

2.1. Preparation of catalysts

In a typical experiment, in order to synthesize Ti–ZrO₂, 1 g of zirconium hydroxide [Zr(OH)₄] (Sigma-Aldrich) is added to a solution of 500 μmol titanium(IV)tetra-2-propoxide [Ti(PrO)₄] (Fluka) dissolved in toluene. Then, the suspension was stirred until the solvent is completely dry and calcined at 500 °C for 2 h.

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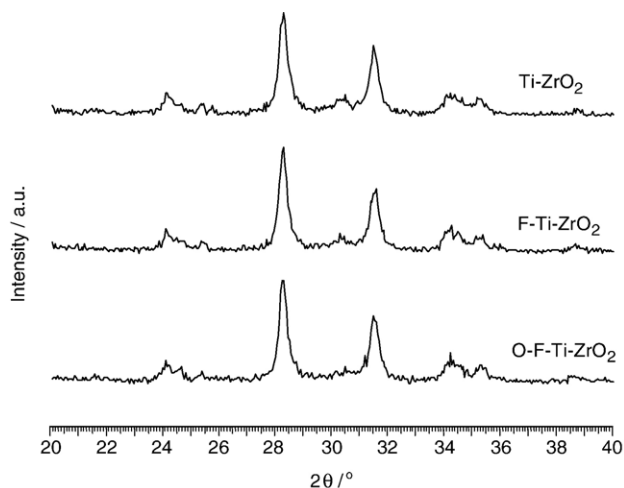


Fig. 1. X-ray diffractograms of Ti-ZrO₂, F-Ti-ZrO₂ and O-F-Ti-ZrO₂.

The fluorination of Ti-ZrO₂ series was carried out by immersing Ti-ZrO₂ into 1 M ammonium hexafluorosilicate [(NH₄)₂SiF₆] (Aldrich) solution for 10 min and then dried at 383 K overnight to give F-Ti-ZrO₂. The F-Ti-ZrO₂ was then further modified by alkylsilylation of octadecyltrichlorosilane (OTS, Aldrich) to yield O-F-Ti-ZrO₂.

Alkylsilylation process was carried out according to the method reported previously [5,6]. In a typical experiment, 1 g of F-Ti-ZrO₂ was suspended in 10 ml of toluene solution containing 500 μmol of OTS. Then, the suspension was centrifuged in order to remove excessive unreacted OTS and washed with toluene and ethanol. The precipitate was then dried at 383 K overnight. Hence, the particles obtained were labeled O-F-Ti-ZrO₂.

2.2. Characterizations

The Ti-ZrO₂, F-Ti-ZrO₂ and O-F-Ti-ZrO₂ were characterized by UV-Vis Diffuse Reflectance (UV-Vis DR), X-ray

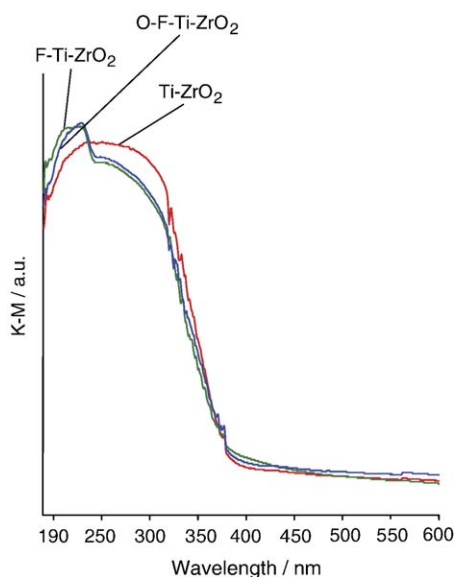


Fig. 2. UV-Vis DR spectra of Ti-ZrO₂, F-Ti-ZrO₂ and O-F-Ti-ZrO₂.

diffraction (XRD), Energy Dispersive X-Ray Analysis (EDAX) and surface area analyzer. UV-Vis spectra were recorded using Perkin Elmer Lambda 900 spectrometer. XRD patterns were acquired on a Bruker D8 Advance instrument using Cu K_α radiation ($\lambda=1.5418 \text{ \AA}$, 40 kV, 40 mA). Surface area of the catalysts was analyzed using BET surface area analyzer instrument (Thermo Finnigan Qsurf Series). Fluorine element in the catalysts was analyzed with EDAX Philips XL 40 instrument at 20 kV.

Hydrophobicity of catalysts was also analyzed by using water adsorption technique. In a typical experiment, the catalysts were dried in an oven at 383 K for 24 h to remove all the physically adsorbed water. After dehydration, the sample was exposed to water vapor at room temperature, followed by the determination of the percentage of adsorbed water as a function of time.

2.3. Catalytic test

To examine the activity of the catalysts, the epoxidation of 1-octene by using aqueous H₂O₂ was chosen as a model reaction. In the epoxidation reaction, 1-octene (4 ml, Aldrich), 30% aqueous H₂O₂ (1 ml, Hanns) and catalyst powder (50 mg) were placed in a glass tube, and the reaction was performed with stirring for 24 h at ambient temperature. The resulting product was withdrawn and analyzed periodically with gas chromatograph (GC). Gas chromatograph-mass spectrometer (GC-MS) was also used to verify the resulting product.

3. Results and discussion

3.1. Physical properties of catalysts

Fig. 1 shows the XRD patterns of ZrO₂, Ti-ZrO₂, F-Ti-ZrO₂ and O-F-Ti-ZrO₂. It is demonstrated that all the modified catalysts possess a similar crystalline structure which is corresponded to monoclinic phase of ZrO₂ [7,8]. This result indicates that ZrO₂ is highly stable to fluorination and alkylsilylation processes.

Fig. 2 shows UV-Vis DR spectra of Ti-ZrO₂, F-Ti-ZrO₂ and O-F-Ti-ZrO₂. The band in the range of 200–240 nm is attributed to a charge-transfer of the tetrahedral titanium sites between O²⁻ and the

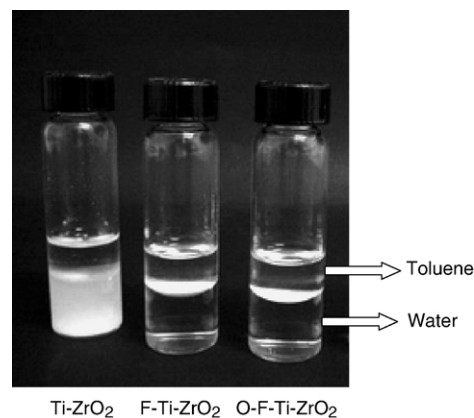


Fig. 3. The photographs showing the distribution of Ti-ZrO₂, F-Ti-ZrO₂ and O-F-Ti-ZrO₂ in the mixture of toluene-water.

central Ti(IV) atoms, while octahedral Ti was reported to appear at around 260–330 nm [9]. ZrO_2 also shows UV absorption bands in the range 200–240 nm as reported previously [10], causing the difficulty to distinguish zirconium species peaks with titanium species peaks in UV–Vis DR spectrum of Ti– ZrO_2 . However, it shows that, for samples containing fluor (F–Ti– ZrO_2 and O–F–Ti– ZrO_2), a single high intense band at around 208 nm can be observed. This band is attributable to titanium in the tetrahedral structure. The decrease in intensity in the range of 260–330, which is corresponded to the octahedral titanium, indicates the occurrence of the transformation of some of the octahedral titanium framework to the tetrahedral structure during the fluorination. The surface area of Ti O_2 – ZrO_2 ($30 \text{ m}^2 \text{ g}^{-1}$), F–Ti– ZrO_2 ($29 \text{ m}^2 \text{ g}^{-1}$) is almost similar to that of O–F–Ti– ZrO_2 ($28 \text{ m}^2 \text{ g}^{-1}$) suggesting that there is no effect of fluorination and alkylsilylation on the surface area of the catalysts. The highly stable properties of ZrO_2 contribute to unaltered surface area as shown by a similar crystallinity of the modified ZrO_2 (see XRD spectra in Fig. 1).

The dispersion behavior of Ti– ZrO_2 , F–Ti– ZrO_2 and O–F–Ti– ZrO_2 in immiscible organic–water mixture is shown in Fig. 3. It is clearly observed that after fluorination and alkylsilylation, the resulting modified particles (O–F–Ti– ZrO_2 and F–Ti– ZrO_2) seemed hydrophobic; some particles were located at the liquid–liquid phase boundary while unmodified Ti– ZrO_2 was dispersed in water. However, after a few minutes, the F–Ti– ZrO_2 was located in the aqueous phase, whereas O–F–Ti– ZrO_2 was still located at liquid–liquid phase boundary due to its hydrophobicity in nature. This observation was supported by water adsorption experiment result. As shown in Fig. 4, it was clearly observed that the amount of adsorbed water on modified Ti– ZrO_2 follows the following trend: Ti– ZrO_2 > F–Ti– ZrO_2 > O–F–Ti– ZrO_2 . It is suggested that fluor and alkylsilyl groups prevent water from adsorbing on the surface of Ti– ZrO_2 . Apparently, the fluorination and alkylsilylation led to changes in hydrophobicity of Ti– ZrO_2 .

The EDAX analysis is a complimentary analysis to check whether the composition of desirable component exists or not in the catalyst since only semi-quantitative result could be obtained using this analysis method. It is calculated that the amounts of zirconium (Zr) and carbon (C) are ca. 55.4 and 19.5 wt.% in O–F–Ti– ZrO_2 , in which carbon originates from alkylsilyl group attached on the surface of the sample. The amounts of titanium (Ti) and silicon (Si) show only ca. 4.0 and 2.0 wt.%, respectively. Fluorine (F) was observed only ca. 1.0 wt.%. This result showed that the amount of fluorine in O–F–Ti– ZrO_2 is very

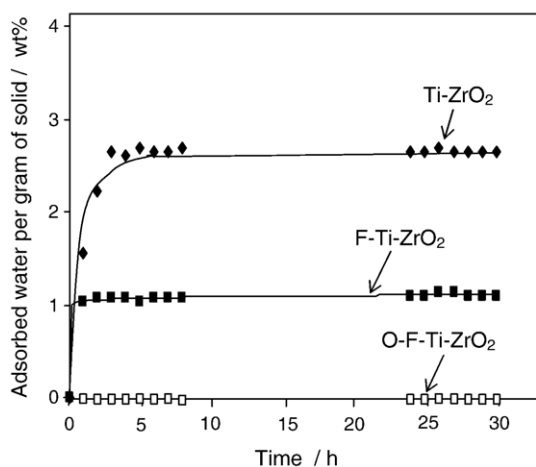


Fig. 4. Percentage of adsorbed water on the surface of Ti– ZrO_2 , F–Ti– ZrO_2 and O–F–Ti– ZrO_2 .

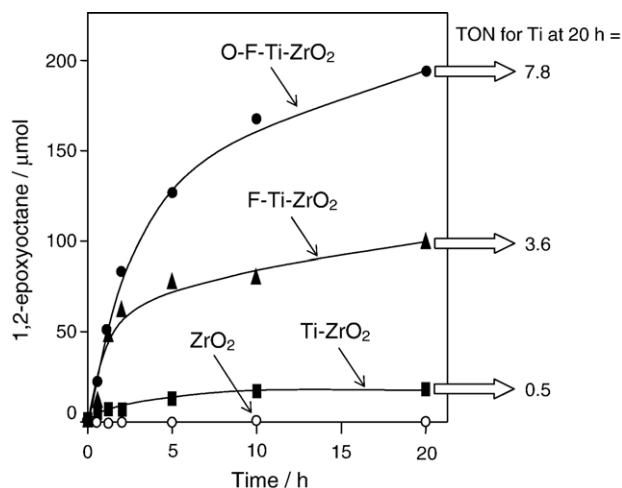


Fig. 5. The epoxidation rate of 1-octene using Ti– ZrO_2 , F–Ti– ZrO_2 and O–F–Ti– ZrO_2 . All reactions were carried out at room temperature for 20 h with 1-octene (4 ml), 30% H_2O_2 (1 ml) and catalyst (50 mg) with stirring.

much lower compared to the amount of ammonium hexafluorosilicate added during the fluorination process (ca. 28%). This suggests that only 1.0 wt.% of fluor is adequate to increase the hydrophobicity of Ti O_2 – ZrO_2 .

3.2. Catalytic activity

A considerable increase in epoxide yield was observed when the surface of Ti– ZrO_2 was fluorinated and alkylsilylated with ammonium hexafluorosilicate and OTS, respectively (see Fig. 5). This phenomenon may be explained in terms of the local environment of Ti active site. As described previously, the difference in the UV–Vis DR spectra of Ti– ZrO_2 , F–Ti– ZrO_2 and O–F–Ti– ZrO_2 samples is due mainly to coordination of titanium on the surface of ZrO_2 . It is generally accepted that isolated Ti(IV) in tetrahedral form are considered the most active species in epoxidation reaction [1–4,11]. Based on these facts, the effect of fluorination on increasing the epoxidation activity of F–Ti– ZrO_2 and O–F–Ti– ZrO_2 can be explained by the presence of isolated Ti(IV) in tetrahedral form.

The increase in epoxidation activity after alkylsilylation can be explained on the basis of an increase in the hydrophobicity of O–F–Ti– ZrO_2 and F–Ti– ZrO_2 catalysts. When the substrates make an interaction to the active sites on the titanium active sites, the H_2O_2 will release water as a side product. The hydrophobic fluor and long carbon chains of alkylsilyl groups will prevent the water to interact with titanium active sites. If this occurs, titanium active sites will be poisoned by water molecules and it might reduce the catalytic activity.

In order to check the regenerability of the catalyst, the recovered and dried O–F–Ti– ZrO_2 was reused in fresh 1-octene and aqueous H_2O_2 . A negligible decrease in the amount of epoxide could be seen. This suggests that epoxide formation does not occur from any leached Ti species. Although the turnover number (TON), the molar ratio of the epoxide to the loaded Ti, was less than one for the reaction with Ti– ZrO_2 , O–F–Ti– ZrO_2 gave a TON of ca. 8, indicating catalytic action of the Ti species (see Fig. 5).

4. Conclusion

The results described above indicate that the catalytic properties of Ti O_2 – ZrO_2 (Ti– ZrO_2) fluorinated Ti O_2 – ZrO_2

(F–Ti–ZrO₂) and alkylsilylated F–TiO₂–ZrO₂ (O–F–Ti–ZrO₂) exist due to the presence of titanium active sites on their surface. The increases in catalytic performance of F–Ti–ZrO₂ and O–F–Ti–ZrO₂ were brought about by fluorination and alkylsilylation processes of Ti–ZrO₂. It is demonstrated that the fluorination can change the coordination of Ti active sites from octahedral to tetrahedral and also increase the hydrophobicity of the catalyst. Alkylsilylation on the other side has absolutely increased the catalyst hydrophobicity. As expected, the catalytic activity of F–Ti–ZrO₂ increases significantly in the epoxidation of 1-octene with aqueous hydrogen peroxide. In conclusion, the high activity of O–F–Ti–ZrO₂ can be considered as the influence of its hydrophobicity and also nature of the active sites on their surface.

Acknowledgments

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