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SHORT COMMUNICATION

PREPARATION OF TRANSPARENT TS-1 ZEOLITE FILM AND ITS PHOTOCATALYTIC ISOMERIZATION UNDER UV IRRADIATION

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Abstract – TS-1 zeolite film has been prepared by using nano sized TS-1 zeolite particles for the photocatalytic isomerization of *cis*-2-butene. TS-1 zeolite film showed optical transparent property and the thickness of film was 0.7 μm. UV irradiation of TS-1 zeolite film in the presence of *cis*-2-butene leads to the photocatalytic isomerization of *cis*-2-butene into *trans*-2-butene at the temperature of 275 K. The yield of *trans*-2-butene was linearly increased with UV-irradiation time.

Key words : Transparent Film, TS-1, Photocatalyst, Geometric Isomerization

INTRODUCTION

Many chemical processes involving large polyatomic compounds include isomerizations and decompositions. Some of these are of great practical importance, for example, the decomposition and isomerization of large organic radicals in combustion environments. Among the isomerization method, photocatalytic isomerization is expected to be a novel key technology in many chemical processes involving large polyatomic compounds in combustion environments [Ichihashi et al., 1996]. However, there have been few investigations on photocatalytic isomerization of butenes. Up to now, Anpo and co-workers studied the photocatalytic isomerization of 2-butene on ZrO_2 and MgO [1989]. Recently, it has been reported that zeolite (metallosilicate) is active in the photocatalytic reaction, since zeolite with well-defined nano pore structure provides modified spaces for photocatalyst [Inui et al., 1992]. However, only powder type of zeolite was used for photocatalytic reaction. For advanced application of zeolite for photocatalytic reaction, it is needed to change the morphology of zeolite powder into the film.

In our previous work, we synthesized nano sized TS-1 zeolite particles under mild conditions to control the particle size (1 atm, 353 K) [Kiyozumi et al., 1996; Jung et al., 1996a]. We have tried to make the zeolite film from the nano sized TS-1 zeolite particles for photocatalytic reaction [Jung et al., 1996a]. Tsapasis et al. synthesized nano sized zeolite L and formed transparent zeolite L film on the petri dish from the colloidal suspension [1995]. However, up to now, there is no report on the preparation of optically transparent TS-1 zeolite film and its applications for photocatalytic reaction.

In this paper, we report the morphological change of zeolite particle into transparent TS-1 zeolite film for photocatalytic reaction. The photocatalytic isomerization of *cis*-2-butene under UV irradiation was studied.

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EXPERIMENTAL

The nano sized TS-1 zeolite was crystallized in the condition of 353 K and 1 atm by the method reported in our previous papers [Kiyozumi et al., 1996; Jung et al., 1996a]. Particle size and crystallinity of TS-1 zeolite were measured by using dynamic light scattering (DLS) method and X-ray diffraction (XRD, Rigaku) using CuKα radiation (λ=1.5405 nm), respectively. After crystallization at 353 K, TS-1 zeolite having 80-90 nm in size was obtained and the crystallinity of the TS-1 zeolite was more than 95 %. After separating the TS-1 crystals from mother liquid by centrifugation, they were redispersed in de-ionized water. When TS-1 zeolite particles were dispersed in de-ionized water, there was no precipitation due to the Brownian motions of nano sized TS-1 particles [Yan et al., 1995]. TS-1 zeolite film was formed on the surface of micro slide glass by dipping the micro slide glass into the dispersed TS-1 solution and drying the solution at 373 K. To remove organic molecule, TPAOH, the TS-1 zeolite film was calcined at 823 K for 2 h.

The photocatalytic isomerization of *cis*-2-butene was carried out with TS-1 zeolite film as prepared in a quartz cell with flat bottom connected to a conventional vacuum system (10^{-6} torr range). The TS-1 zeolite film was degassed at 725 K for 2 h, heated in O_2 at the same temperature for 2 h, and finally outgassed at 475 K to 10^{-6} torr prior to use in photo reactions and spectroscopic measurements [Moon et al., 1995; Anpo et al., 1989]. UV-irradiation to the catalyst in the presence of *cis*-2-butene was carried out using a 75-W high-pressure Hg LAMP (λ> 280 nm) at 275 K. The reaction products were analyzed by a gas chromatograph. The UV-visible reflectance spectra were obtained using a Varian Cary 2200 spectro-photometer.

RESULTS AND DISCUSSION

1. Preparation of TS-1 Zeolite Film

Fig. 1 shows XRD pattern of the TS-1 zeolite film obtained. It shows that the TS-1 zeolite film has MFI-type structure with an orthorhombic symmetry. After calcination at 823 K, apparently there was no crack on the surface of the TS-1 zeolite film and the film showed optical transparency. To investigate the surface and the fracture morphology of the zeolite film, scanning electron microscopy (SEM) was applied. In Fig. 2a, it clearly shows that TS-1 particles with the size of 80 nm was well packed on the surface of micro slide glass. Sano et al. have suggested that opaque zeolite film could be made with zeolite particles of 3-5 μm in diameter by the intergrowth among the zeolite primary particles under the hydrothermal synthesis condition [1992]. The opaqueness may stem from the large particle size of 3-5 μm in diameter. From the nano range ceramic particles, Daganis suggested that fairly transparent ceramic disk could be obtained because these samples did not scatter much light due to the size [1992]. In our case, the transparent property of the zeolite film resulted from the use of nano sized TS-1 zeolite [Jung et al., 1996b], and could be applicable to the advanced optical materials for photo catalysis, optical switching, hole burning, and laser focusing [Alivisatos et al., 1988]. Fig. 2b shows SEM image of the fracture of the zeolite film coated on the micro slide glass after calcination at 823 K. As shown in the SEM image, the thickness of zeolite film was about 0.7 μm and TS-1 zeolite particles with about 80 nm were densely packed on the surface of the micro slide glass to form film.

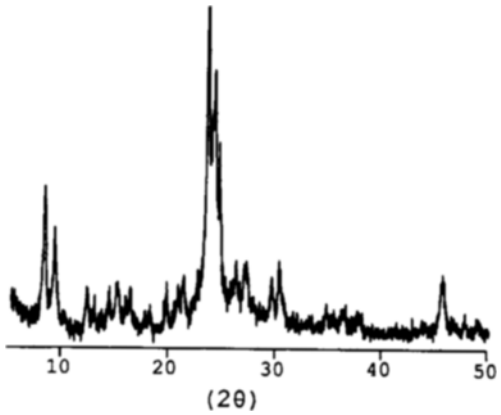


Fig. 1. X-ray diffraction (XRD) pattern of TS-1 zeolite film as prepared.

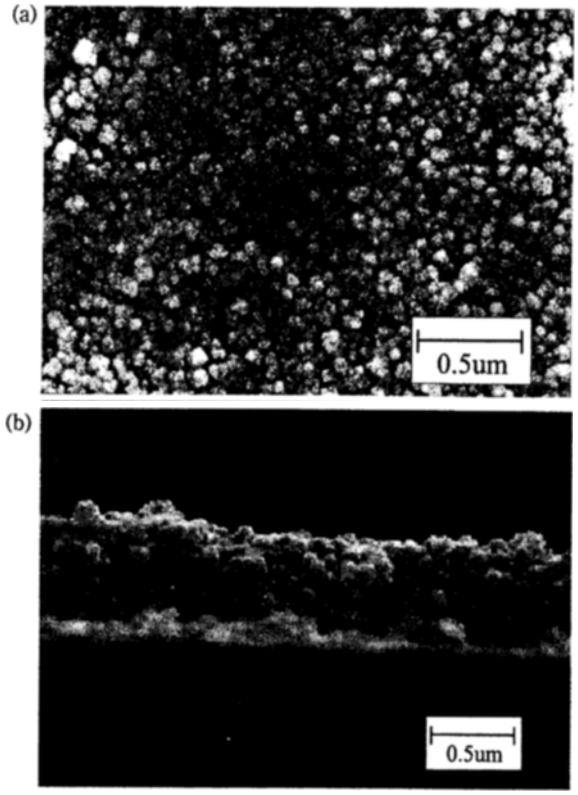
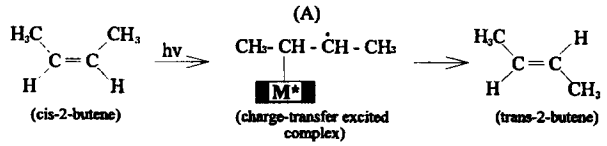


Fig. 2. Scanning electron micrographs of the surface (a) and the fracture (b) of TS-1 zeolite film.

2. Isomerization of *cis*-2-Butene

The photocatalytic isomerization of butene has been the subject of many studies. Photocatalytic isomerization of *cis*-2-butene into *trans*-2-butene over TS-1 zeolite film is shown in Fig. 3. UV irradiation of the TS-1 zeolite film in the presence of *cis*-2-butene at 275 K was found to lead to the efficient formation of *trans*-2-butene (geometrical isomerization). The formation of 1-butene, i.e., double-bond shift isomerization, was minor reaction. The yield of *trans*-2-butene was linearly increased with UV irradiation time. Anpo et al. have reported that the yield of *trans*-2-butene was linearly increased with UV irradiation to degassed MgO sample [1989]. The photocatalytic isomerization of *cis*-2-butene to *trans*-2-butene on an MgO catalyst proceeds via a mechanism similar to that proposed for metal oxides such as TiO_2 and supported V_2O_5. *cis*-2-butene transforms by UV irradiation to charge-transfer excited complex (A) resulting in the opening of the C=C double, which participates in geometric isomerization to *trans*-2-butene. The charge-transfer excited state of the low coordinated surface site plays a significant role in the reaction.



In our case, the coordination number of titanium might be important role in the photocatalytic isomerization. DRS-UV spectroscopy has been applied to probe the existence of framework and nonframework titanium. The band at 220 nm, the broad shoulder around 270 nm, and the band at 310 nm were assigned to isolated framework titanium in tetrahedral coordination, the nonframework titanium, and the anatase structure, respectively [Nizamidin and Tatsumi, 1996]. The DRS-UV spectrum for the TS-1 zeolite film is shown in Fig. 4. TS-1 film exhibits one absorption band at 220 nm. From the DR-UV results, it is evident that the TS-1 film is free of nonframework titanium. The absence of band between 310 nm and 350 nm indicates that anatase like phase was not formed in the TS-1 zeolite film. This results suggest that tetrahedrally coordinated titanium is mainly involved in the geometric isomerization. The interaction

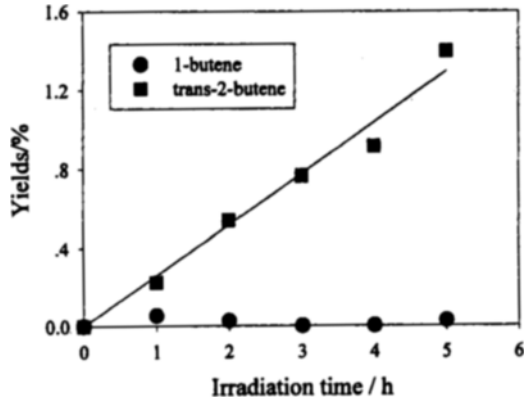


Fig. 3. Time profile of the photocatalytic isomerization of *cis*-2-butene over TS-1 zeolite film.

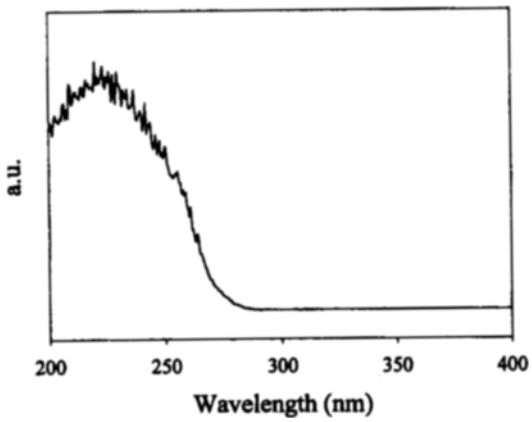


Fig. 4. DR-UV spectrum of TS-1 zeolite film.

of *cis*-2-butene with the charge transfer excited state, $(Ti^{3+}\text{--}O^{-})^*$, results in the opening of its C=C double bond which in turn results in the geometrical isomerization into *trans*-2-butene in a similar manner to the photocatalytic reaction on MgO powder. At the reaction temperature (275 K) thermal isomerization scarcely proceeded and the reaction yield was negligible as compared to photocatalytic isomerization.

From the results it is concluded that transparent TS-1 zeolite film showed photocatalytic activity over geometric isomerization of *cis*-2-butene into *trans*-2-butene and the possibility of application of zeolite film for photocatalytic reaction. It could open a new application of TS-1 zeolite film in photocatalytic conversion of hydrocarbon.

NOMENCLATURE

λ : wavelength
h : Planck constant
ν : frequency
h : time [hour]

Greek Letter
θ : angle

Superscript
* : excited state

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