

The Photocatalytic Isomerization of 2-Butenes on ZrO₂ Catalyst with Low Coordinated Surface Sites

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The photocatalyzed isomerization of *cis*-2-butene has been investigated on active ZrO₂ catalysts which exhibited a typical photoluminescence associated with low coordinated surface sites. A geometrical isomerization reaction occurred predominantly and with high efficiency under UV-irradiation of the ZrO₂ catalyst in the presence of *cis*-2-butene. A good parallel between the photoluminescence intensity and the rate of photocatalytic activity clearly indicated that the low coordinated surface sites play a significant role in the photocatalytic isomerization of *cis*-2-butene on the active ZrO₂ catalysts.

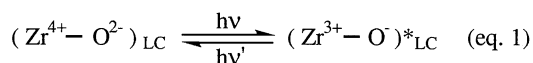
It is well established that surface ions at positions of coordinative unsaturation play a significant role in heterogeneous catalysis. Such low coordinated surface sites are also known to play a vital role in the appearance of abnormal absorption and photoluminescence bands in insulating materials with a high surface area such as powdered MgO and SrO.¹ We have recently reported that well-degassed ZrO₂ catalysts which have an efficient reactivity for the hydrogenation of CO and ethylene exhibited a typical photoluminescence associated with low coordinated surface sites similar to those for MgO powders.^{2,3}

On the other hand, the catalytic isomerization reactions of butenes has been the subject of many studies.^{4,5} However, there has been few investigations on photocatalytic isomerization reactions of butenes.⁶ Therefore, it is worthwhile to investigate the photocatalytic possibility of active ZrO₂ catalysts for the isomerization of *cis*-2-butene and to clarify the role of low coordinated surface sites in the photocatalytic reactions.

The ZrO₂ catalyst was prepared by the precipitation of a ZrO(NO₃)₂ solution with NH₄OH, as previously reported,³ and by calcination of the precipitate in air at 773 K for 5 h. The photoluminescence spectra of the catalyst were measured at 77 K using a Shimadzu RF-501 spectrophotofluorometer. The photocatalytic isomerization of *cis*-2-butene was performed in a quartz cell (50 ml) connected to a vacuum system. Prior to the photocatalytic reactions, the catalyst (0.5 g) was degassed for 2 h at the desired temperature. The reactant gas was then introduced into the quartz reactor. UV-irradiation of the catalyst in the presence of *cis*-2-butene (6 Torr) was carried out with a high-pressure Hg lamp at 275 K. The reaction products were collected at defined reaction intervals and analyzed by gas chromatography.

Figure 1 shows the photoluminescence spectrum of the active ZrO₂ catalyst degassed at higher temperatures. The active ZrO₂ catalyst exhibited a photoluminescence spectrum at around 420–550 nm with the excitation wavelength at 280–330 nm which coincided with that of the absorption band observed in UV-VIS absorption measurements.² This photoluminescence spectrum was observed with a detectable intensity only when the sample was exhaustively degassed at temperatures higher than 573 K. The photoluminescence was then efficiently and completely quenched by the addition of hydrogen and oxygen. These results suggest that the appearance of the photoluminescence spectrum of the well-evacuated ZrO₂ catalyst may be attributed to the

charge-transfer processes over low coordinated surface sites (eq. 1):



LC: low coordination

As shown in Fig. 2-a, the photoluminescence intensity attributed to the low coordinated surface sites depends a great deal on the degassing temperatures. The intensity increases gradually with the degassing temperatures and reaches a maximum at around 1073 K, then slightly decreases at higher temperatures because of the annealing of the low coordinated surface sites.

Figure 1 also shows the effect of *cis*-2-butene addition on the photoluminescence spectrum of the active ZrO₂ catalyst obtained in this way. As shown in Fig. 1 (b-d), the addition of *cis*-2-butene onto the active ZrO₂ catalyst leads to the efficient quenching of the photoluminescence spectrum of the active ZrO₂ catalyst. With increasing the amount of *cis*-2-butene adsorbed, the photoluminescence spectrum markedly decreased in its intensity and at the same time its lifetime was shortened. After the quenching of the photoluminescence with the addition of *cis*-2-butene, the evacuation of the system at 295 K led to a partial recovery of the original intensity of the photoluminescence (Fig. 1-e). These findings clearly indicate that the charge-transfer excited state of the low coordinated surface sites on the active ZrO₂ catalysts easily interact with the added *cis*-2-butene.

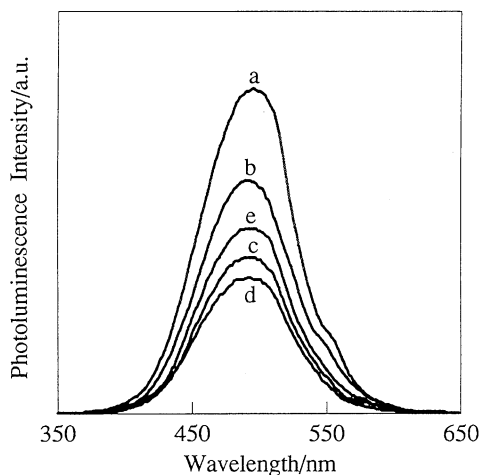


Figure 1. Photoluminescence spectrum of the active ZrO₂ catalyst degassed at 1073 K and the effect of the addition of *cis*-2-butene on the photoluminescence spectrum (recorded at 77 K); (a) photoluminescence spectrum of the active ZrO₂ catalyst, (b-d) after the addition of *cis*-2-butene onto the spectrum (a), b: at 0.1 Torr, c: at 1.0 Torr, d: at 10.0 Torr, (e) after the evacuation of *cis*-2-butene (to 10⁻⁵ Torr).

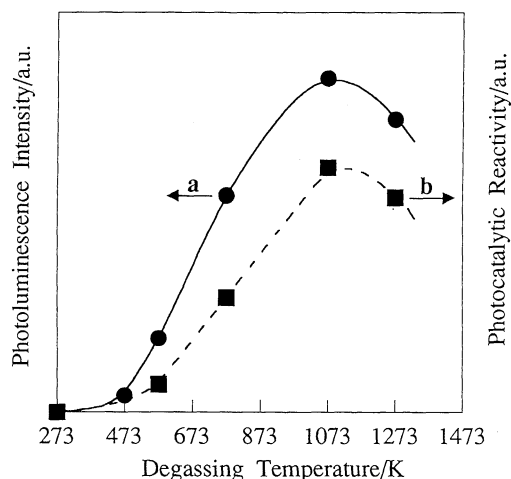


Figure 2. The effect of the degassing temperatures of the ZrO_2 catalyst on the photoluminescence intensity (a) and the photocatalytic reactivity for the isomerization of cis-2-butene at 275 K (b).

UV-irradiation of the active ZrO_2 catalyst in the presence of cis-2-butene at 275 K was found to lead to the efficient formation of trans-2-butene (geometrical isomerization), as well as the formation of a small amount of 1-butene (double bond shift isomerization) ($\text{trans}/(\text{trans}+1)=0.91$, at 30 min of reaction time). Figure 3 shows the effect of UV-irradiation for the photocatalytic isomerization of cis-2-butene on the ZrO_2 catalysts. UV-irradiation of the ZrO_2 catalyst in the presence of cis-2-butene caused the isomerization reaction to proceed immediately and efficiently, its yield increasing linearly with the irradiation time. As soon as UV-irradiation ceased, the isomerization reaction stopped. At the reaction temperatures (275 K), thermal isomerization reaction scarcely proceeded and the reaction yield was negligible as compared to photocatalytic isomerization reactions. Furthermore, the dependence of the isomerization reactivity on the wavelength of the excitation-light was also investigated by changing the color filters. The UV light most effective to the isomerization reaction was observed at the wavelength region of 270–300 nm, which coincided with that of the absorption band of the active ZrO_2 catalyst. These findings suggest that the photocatalytic isomerization reaction of cis-2-butene occurs efficiently and effectively on the active ZrO_2 catalyst.

It was also found that the photocatalytic reactivity of the active ZrO_2 catalysts strongly depended on the degassing temperature. Figure 2-b shows the dependence of the photocatalytic reactivity for the isomerization of cis-2-butene on the degassing temperatures as well as for the photoluminescence yield of the

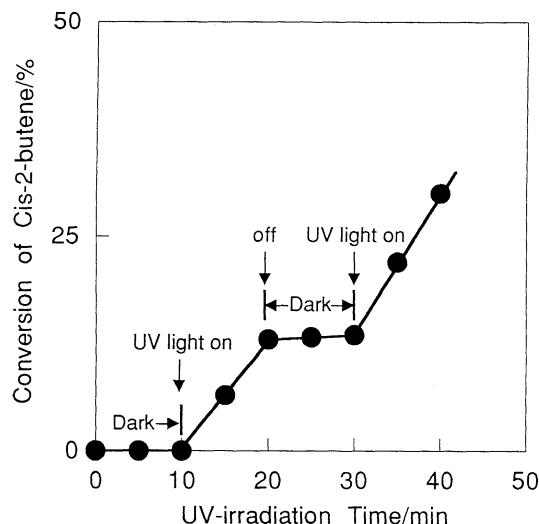


Figure 3. The effect of UV-irradiation on the isomerization of cis-2-butene on the active ZrO_2 catalyst at 275 K.

catalysts (Fig. 2-a). As shown in Fig. 2, the photocatalytic reactivity corresponds well with the photoluminescence yield of the catalysts, directly indicating that the charge-transfer excited state of the low coordinated surface sites plays a significant role in the photocatalyzed isomerization reaction.

From these results it can be concluded that the interaction of cis-2-butene with the low coordinated surface sites of the active ZrO_2 catalyst in their charge-transfer excited state occurs smoothly and the interaction of cis-2-butene with the charge-transfer excited state of the $[\text{Zr}^{3+} - \text{O}]^*$ pair state results in the opening of its $\text{C}=\text{C}$ double bond which in turn result in the geometrical isomerization of cis-2-butene into trans-2-butene in a manner similar to the photocatalytic isomerization of 2-butene on well-degassed MgO powders.

References

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