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Selective Dimerization and Hydrogenation of Ethylene on Active Zirconium Oxide with Coordinatively Unsaturated Surface Sites

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The evacuation of the ZrO_2 catalyst at higher temperatures led to the appearance of an abnormal absorption and photoluminescence due to the formation of coordinatively unsaturated surface sites. These active ZrO_2 catalysts having coordinatively unsaturated surface sites exhibited a high catalytic activity for the selective dimerization of C_2H_4 to 2-C_4H_8. In the presence of H_2 and C_2H_4, the formation of C_4H_{10} was observed in place of 2-C_4H_8. The significant role of the coordinatively unsaturated surface sites in these reactions on the active ZrO_2 catalyst has been clarified in detail for the first time.

The activation of H_2 on the catalyst surface is vital with regard to hydrogenation reactions. Recently, Domen et al.[1)] have reported that ZrO_2 catalysts prepared from $ZrO(NO_3)_2$ exhibit a specific activity in the hydrogenation of CO and C_2H_4. By applying a dynamic photoluminescence technique to these catalysts, we have observed that coordinatively unsaturated surface sites (CUS) are generated on the active ZrO_2 surface by evacuation at temperatures higher than 673 K, which subsequently play a significant role in the dissociative adsorption of H_2 and CO.[2)] Such CUS were also found to be instrumental in the appearance of abnormal absorption and photoluminescence bands as well as in the dissociative absorption of H_2 and also in catalytic reactions on alkali-earth metal oxides such as MgO and SrO.[3)]

On the other hand, some metal and metal oxide catalysts supported on SiO_2 are known as active catalysts for the dimerization of alkenes.[4,5)] However, in the hydrogenation of alkenes, some pure metal oxide catalysts such as NiO, ZnO, and Al_2O_3, etc. are known to exhibit a reactivity for the hydrogenation of C_2H_4, but not for dimerization.[6,7)]

In this paper, active ZrO_2 catalysts having CUS are discussed along with observations of the selective dimerization of C_2H_4 to 2-C_4H_8 in the presence of C_2H_4 alone as well as the hydrogenation of C_2H_4 to C_2H_6 and C_4H_{10} in the presence of a mixture of C_2H_4 and H_2 on the active ZrO_2 catalysts at 298 K, respectively.

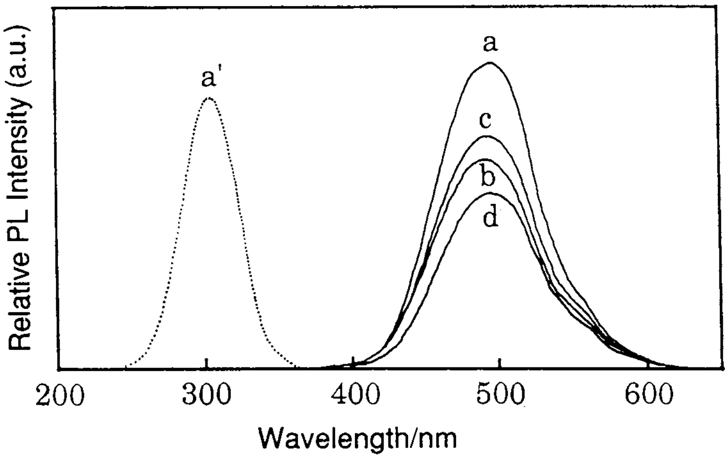

Fig. 1. Photoluminescence spectrum (PL) of the active ZrO_2 catalyst and the effect of the addition of the reaction gases onto the PL spectrum (recorded at 77 K). a: PL spectrum of the active ZrO_2, b: after the addition of C_2H_4 (18 Torr), c: after the evacuation of C_2H_4 (to 10^{-6} Torr), d: after the addition of H_2 onto the spectrum (c) (20 Torr).

The ZrO_2 catalysts were prepared by the precipitation of the $ZrO(NO_3)_2$ solution with NH_4OH after which the precipitates were dried and calcined in oxygen at 773 K. Before recording the photoluminescence spectra, the ZrO_2 catalyst was degassed for 9 h at the desired temperature in the region of 300 to 1173 K. The photoluminescence spectra (PL) of the catalyst were recorded at 77 K with a Shimadzu RF-501 spectrofluorophotometer. Prior to the catalytic reactions, the ZrO_2 catalyst was evacuated at 1073 K for 9 h. The effluent gases were analyzed by gas chromatography.

Figure 1 shows the typical PL (solid line: a) and its excitation spectrum (i. e., absorption spectrum) (dotted line: a') of the ZrO_2 catalyst evacuated at 1173 K. It also shows the effect of the addition of C_2H_4 on the PL. It has been confirmed that before evacuation at high temperatures, the ZrO_2 catalyst never shows any absorption and PL. The ZrO_2 catalyst exhibits the PL and absorption bands only after treatment at temperatures higher than 600 K in vacuum, their intensities strongly depending on the evacuation temperature and time. These absorption and PL spectra are attributed to the following charge transfer processes on the CUS:

$$(Zr^{4+} — O^{2-})_{LC} \underset{h\nu'}{\overset{h\nu}{\rightleftharpoons}} (Zr^{3+} — O^{-})^{*}_{LC} \qquad \text{(eq. 1)} \quad \text{(LC ; low coordination)}$$

As shown in Fig. 1, the addition of C_2H_4 onto the ZrO_2 catalyst leads to the efficient quenching of the PL. After quenching, the evacuation of the system at 298 K leads to only a partial recovery of the original intensity of the PL, i. e., a reversible quenching, while most of the intensity remains unrecovered, i. e., an irreversible quenching of the PL. Thus, both the reversible and irreversible quenchings of the PL were observed with the addition of C_2H_4. These findings clearly suggest that the added C_2H_4 easily interacts with the CUS exhibiting at least two different interactions, one weak and reversible and the other strong and irreversible.

Table 1. The Yield of the Products in the Reactions of the Dimerization of C_2H_4 and the Hydrogenation of C_2H_4 with H_2 on the Active ZrO_2 Catalyst (μmol/g-cat.)

reactants / amount of C_2H_4	only C_2H_4		C_2H_4 + H_2 a)		only s-π-C_2H_4 + H_2 b)		H_2 + C_2H_4 c)	
	product	yield	product	yield	product	yield	product	yield
1.82 Torr (6 μmol/ g-cat.)	not detected		C_2H_6	1.96	C_2H_6	15.6	C_2H_6	0.14
92.5 Torr	2-C_4H_8	1.26	C_2H_6 C_4H_{10}	5.01 21.0	C_4H_{10}	22.0	2-C_4H_8 C_4H_{10}	48.9 < 0.1
152 Torr	2-C_4H_8	20.0	C_2H_6 C_4H_{10}	16.2 81.5	C_4H_{10}	30.0	——	

a) H_2 (20 Torr) is added onto the system on which C_2H_4 was preadsorbed at the desired pressures.
b) H_2 is added onto the system on which C_2H_4 was preadsorbed and subsequently evacuated.
c) C_2H_4 is added onto the system on which H_2 was preadsorbed and subsequently evacuated.
d) The reaction products were analyzed at the difined reaction intervalues.
e) The catalytic reactions were carried out at 298 K.

According to a report on the ZrO_2 catalyst by Domen et al.,[8] there are two types of interactions between ethylene and the ZrO_2 surface: a weak adsorption species identified as π-C_2H_4 and a strong adsorption species identified as s-π-C_2H_4. These results on the adsorption of C_2H_4 on the active ZrO_2 catalyst were found to correspond well with the above findings.

Furthermore, Fig. 1 shows that the addition of H_2 onto the catalyst, on which C_2H_4 quenched the PL of the ZrO_2, also leads to additional quenching, suggesting that H_2 interacts with the remaining unsaturated surface sites. In other words, H_2 can adsorb on the sites on which C_2H_4 does not interact. After quenching by the added H_2, the system was evacuated. Only a partial recovery of the original intensity of PL took place, suggesting that H_2 adsorbs irreversibly on the active ZrO_2 catalyst.

Table 1 shows the results of isomerization and hydrogenation of C_2H_4 on the active ZrO_2 catalyst. As shown in Table 1, column 1, no reaction can be observed upon the introduction of C_2H_4 onto the active ZrO_2 catalyst at pressures lower than 1.82 Torr. In this case, no gaseous C_2H_4 was found and a total corresponding amount of 6 μmol/g-cat of C_2H_4 was adsorbed on the catalyst.[9] However, with the addition of C_2H_4 in the regions of 92.5 - 152 Torr, the selective formation of 2-C_4H_8 was observed. (trans/cis ratio = 1.83). As shown in Table 1, column 2, the addition of H_2 onto the ZrO_2 catalyst on which C_2H_4 was preadsorbed at amounts less than 6 μmol/g-cat, led to the selective formation of C_2H_6, while the addition of H_2 on the ZrO_2 catalyst on which C_2H_4 was introduced at pressures higher than 92.5 Torr led to the formation of C_4H_{10} with a minor formation of C_2H_6.

On the other hand, as shown in Table 1, column 3, the addition of H_2 on the ZrO_2 catalysts on which C_2H_4 was preadsorbed at amounts less than 6 µmol/g-cat and on which the gaseous C_2H_4 and weak adsorption species of C_2H_4 were evacuated at 298 K, led to the selective formation of C_2H_6. However, the addition of H_2 on the ZrO_2 catalyst on which C_2H_4 was preadsorbed at pressures higher than 92.5 Torr and on which the gaseous C_2H_4 and weak adsorption C_2H_4 were evacuated at 298 K, led to the selective formation of C_4H_{10}. These results also indicate that gaseous C_2H_4 plays a significant role in the formation 2-C_4H_8 in the absence of H_2 in the system, as well as in the formation of C_4H_{10} in the presence of H_2. Furthermore, it indicates that the formation of C_4H_{10} proceeds via the formation of 2-C_4H_8. In fact, the hydrogenation of 2-C_4H_8 on the active ZrO_2 catalyst was found to be a very facile reaction supporting the above mechanisms.

Table 1 also indicates that a relatively strong adsorption species of C_2H_4 selectively contributes to the formation of C_2H_6. Being in good agreement with results showing that the quenching of the photoluminescence is more efficient with H_2 than C_2H_4, it is clear that the adsorption of H_2 is much stronger than that of C_2H_4. Therefore, as can be seen in Table 1, column 4, the introduction of C_2H_4 at 1.82 Torr and at 92.5 Torr onto the ZrO_2 catalyst on which H_2 was presorbed and gaseous H_2 was evacuated, produced only small amounts of C_2H_6 and C_4H_{10}, respectively. These findings clearly indicate that the strong adsorption hydrogen species do not contribute to the hydrogenation reaction. It can be concluded that only weakly interacting species of hydrogen and C_2H_4 play significant roles in the dimerization and hydrogenation reactions of C_2H_4 on the active ZrO_2 catalyst.

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9) Furthermore, a total amount of 6 µmol/g-cat of C_2H_4 was coincidentally found to correspond to the total number of the LCSS on the ZrO_2 catalyst determined by the quantitative measurement of the PL of the catalyst.

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