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Infrared studies of ethene hydrogenation over ZrO_2

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Hydrogenation of adsorbed ethene over ZrO_2 at low temperature was observed by in situ infrared transmission spectroscopy. It was found that di-hydrogen was directly activated on the site where ethene was already adsorbed, which was confirmed by the comparison of adsorbed species produced during the reaction and adsorbed ethane species.

Keywords: Ethene; hydrogenation; IR spectroscopy; ZrO_2

1. Introduction

Adsorption and hydrogenation of ethene have been intensively investigated for several decades over supported metal catalysts, metal single crystal surfaces and metal oxide catalysts [1–5]. The observed species derived from ethene adsorption on metals are, π-bonded, di-σ-bonded ethene and ethylidyne [6,7]. Although ethylidyne is the most stable species, it is not regarded as an intermediate species during ethene hydrogenation [8–11], and the mechanism for the catalytic ethene hydrogenation still seems to be obscure because of the complicated mechanism over metals. On the other hand, it is known that ethene hydrogenation proceeds over metal oxides rather slowly with less complexity [12–25]. It was first found by Burwell and co-workers over Cr_2O_3 [12–16] that the mechanism of ethene hydrogenation was simpler over metal oxides than over metals. The same conclusion was obtained on ZnO by Kokes and co-workers [20–25] by combination of volumetric method and in situ IR spectroscopy, and they observed the ethyl species during the reaction.

In this study, adsorption of hydrogen [26], ethene [27] and ethane [28] on ZrO_2 was examined by IR spectroscopy. Then the reaction mechanisms were considered based on the analysis of IR spectra of produced species during ethene hydrogenation over ZrO_2.

2. Experimental

ZrO_2 was obtained by precipitation from the oxynitrate solution with NH_4OH and by calcination of the hydroxide at 773 K for 3 hr. Ca. 50 mg of ZrO_2 was pressed into a self-supported disc of 20 mm diameter. The disc was placed in the center of the IR cell which was connected to a Pyrex gas circulation system. The temperature was controlled from 100 to 1073 K and the apparent temperature was corrected to the real temperature by comparison with a thermocouple that was directly attached to a disc inside the cell. Pretreatment of the sample was carried out with 100 Torr of O_2 at 773 K followed by evacuation at 1023 K for 20 min. H_2 gas was refined by passing through a Deoxo tube and liquid N_2 trap. D_2 gas was used after refinement by liquid N_2 trap. Ethene (Takachiho, 99.9% pure) and ethane (Takachiho, 99.9% pure) were refined by vacuum distillation. C_2D_4 (MSD isotopes, 99% atom D) and HD (MSD isotopes, 98.9% atom D) were used without further purification. Isotopes of ethane CH_3CH_2D, CH_2DCH_2D, CHD_2CHD_2, CHD_2CD_3 and C_2D_6 were obtained by hydrogenation at 213 K of either C_2H_4 or C_2D_4 with either H_2, HD or D_2. The possibility of self-hydrogenation or exchange reaction at this low temperature was disregarded as the reaction $(C_2H_4 + D_2)$ was found by NMR to produce only CH_2DCH_2D as initially reported by Burwell and co-workers over Cr_2O_3 [12–16]. Ethene and ethane were introduced to the sample at ca. 5 Torr and were either evacuated or trapped by liquid N_2 before and during the measurement of spectra. Each spectrum was recorded on a JEOL JIR-100 Fourier-transform infrared (FT-IR) spectrometer with a liquid N_2 cooled MCT detector and was taken with 256 scans at a resolution of 4 cm^{-1}. IR spectra of adsorbed species are described as ratio spectra of ZrO_2 with adsorbed species and spectra in vacuum at the same temperatures.

3. Results and discussion

1. HYDROGEN ADSORPTION

On dehydrated ZrO_2 surface after the pretreatment, four different types of hydrogen adsorption are observed as summarized as follows; 1) associated adsorption below 173 K, 2) homolytic dissociative adsorption below 373 K, 3) heterolytic dissociative adsorption between 223 and 373 K, and 4) dissociative adsorption above 300 K. The IR spectra of these species taken below 273 K are shown in fig. 1. At 173 K di-hydrogen species derived from associated adsorption of H_2 is observed at 4029 cm^{-1}, which exists only in the ambient H_2 gas with saturation pressure at ca. 100 Torr. At 173 K temperature $\mathrm{Zr}\begin{smallmatrix}\diagup\mathrm{H}\\ \diagdown\mathrm{H}\end{smallmatrix}$ species due to homolytic dissociative adsorption is also observed as a broad band centered at 1540 cm^{-1}. This adsorption is reversible above 173 K, and the sites for $\mathrm{Zr}\begin{smallmatrix}\diagup\mathrm{H}\\ \diagdown\mathrm{H}\end{smallmatrix}$ species saturates at ca. 5 Torr of H_2 gas. From 223 K heterolytic dissociative adsorption generating ZrH and OH species at 1562 and 3668 cm^{-1} respectively is observed. The heterolytic dissociative adsorption is saturated at

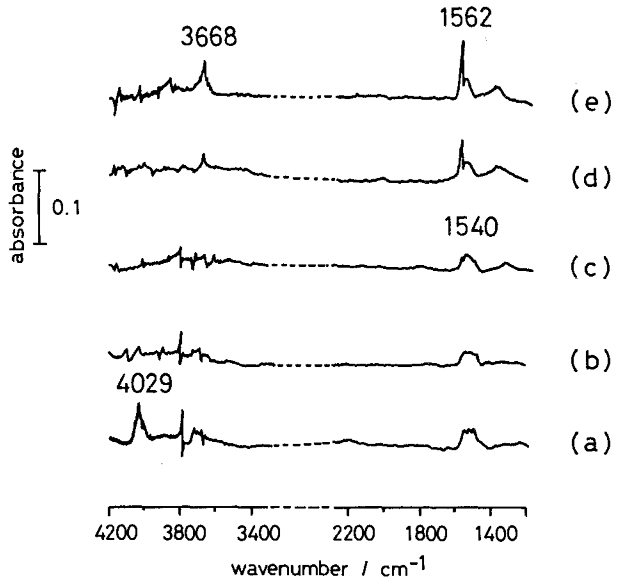


Fig. 1. IR spectra of adsorbed H_2 at various temperatures: (a) 173 K; (b) 203 K; (c) 223 K; (d) 243 K and (e) 273 K.

ca. 400 Torr. Once it takes place, ZrH and OH species are irreversibly observed below 223 K under evacuation. It is also interesting that considerable isotope effect for this adsorption between H_2 and D_2 was observed [26]. Above 300 K another type of dissociative adsorption which produced two different OH species at 3668 and 3778 cm^{-1} is also observed.

2. ETHENE ADSORPTION

In fig. 2 IR spectra of adsorbed ethene on ZrO_2 are presented. Ca. 5 Torr of ethene was introduced to ZrO_2 in each experiment. In a warming procedure ZrO_2 was exposed to ethene at 153 K for ca. 1 min and the gas phase was evacuated before and during IR measurement. The use of liquid N_2 trap for removal of ethene in the gas phase instead of evacuation resulted in the same spectra as those in fig. 2. In a cooling procedure, ethene was introduced at room temperature and the ZrO_2 was cooled in an atmosphere of ethene. The gas phase was trapped only when spectra were taken at each temperature. When warming and cooling procedures were cycled the same spectra were obtained at the same temperature for all procedures of this series, implying that the adsorption of ethene is fully reversible on ZrO_2 surface. Each spectrum in fig. 2 was taken during a procedure of gradual warming.

All the IR bands were reduced in intensity when the sample was warmed, which means the decrease of adsorbed species. If there existed only one adsorbed species, the decreasing rate of all the bands should be the same.

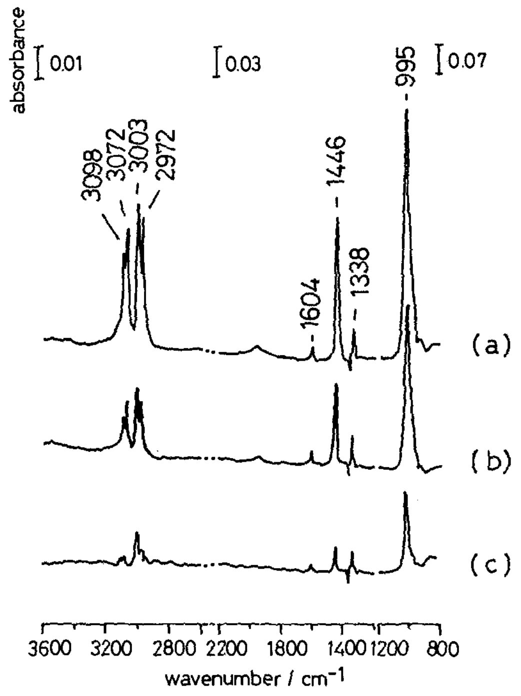


Fig. 2. IR spectra of adsorbed C_2H_4 at various temperatures: (a) 173 K, (b) 208 K and (c) 298 K.

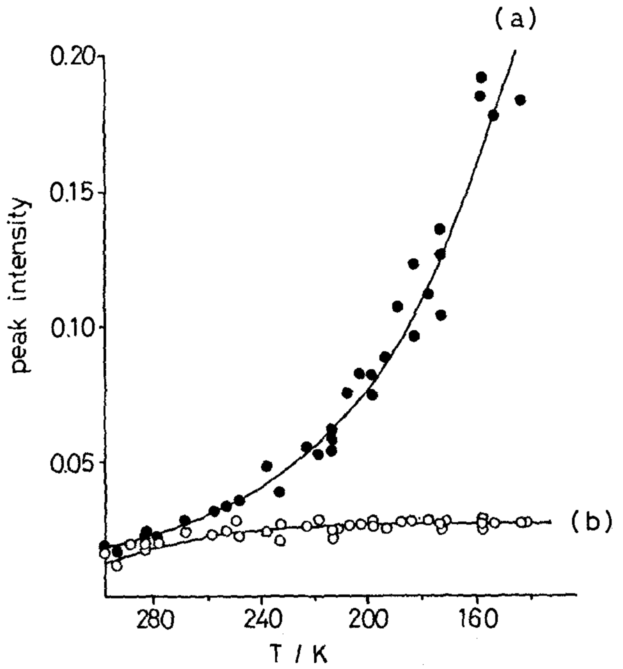


Fig. 3. Dependence of peak intensity of adsorbed C_2H_4 on adsorption temperature; (a) peak intensity of the band at 1446 cm^{-1} and (b) at 1338 cm^{-1}.

However, the rate of decrease among four bands in CH stretching region and among the bands below 2200 cm^{-1} were different. For example, the peak intensities of the bands at 1446 and 1338 cm^{-1} were plotted as a function of adsorption temperature in fig. 3. It is shown that the band at 1446 cm^{-1} increased in intensity as the temperature decreased, while that at 1338 cm^{-1} kept constant below 240 K. Since the decrease rates of two bands in fig. 3 were the same above 260 K, it is considered that there are two different species; one which shows both bands at 1446 and 1338 cm^{-1} above 260 K, and the other which does not involve the band at 1338 cm^{-1}. Both bands at 1446 and 1338 cm^{-1} are assigned to CH_2 scissoring modes [27] and the latter one is IR inactive in gas phase. Therefore the spectrum in fig. 2(c) at 298 K presents strongly(s)-π-bonded ethene with two characteristic bands at 1604 (C=C stretching) and 1446 cm^{-1} which are originally IR inactive. The other species charactherized by four CH stretching bands and the other bands at 1446 and 995 cm^{-1} is regarded as the ordinary π-bonded adsorbed ethene. As the reaction was observed below 193 K, only the ordinary π-bonded ethene was concerned, which is the dominant species at the temperature.

3. ETHANE ADSORPTION

Isotopic analysis of IR spectra to examine the adsorption structure of adsorbed ethane (the product of ethene hydrogenation) were carried out. The IR spectra of adsorbed C_2H_6 are shown in fig. 4. The procedure of spectrum measurements is the same as that for ethene adsorption. Above 193 K only one species was observed keeping the ratio among its IR bands constant. The characteristic point of the adsorbed species above 193 K is that it showed CH stretching bands at very low frequency compared with gas phase ethane and that the bands which are originally IR inactive in gas phase considerably appeared at 1340 (CH_3 s-deformation) and at 993 (C–C stretching). Below 193 K the intensity of each bands increased in different ways gradually as the temperature decreased. This means the appearance of another species. Since the spectrum (c) involves the spectra of both two species, the IR spectrum of the low temperature species was obtained by subtraction of the spectrum (a) from (c) and is described in fig. 4 (d). The spectrum of this species seems to be similar to that of ethane in gas phase. From the behavior and the spectra of two species, it is concluded that the one observed at higher temperature has stronger interaction with the ZrO_2 surface, while the other one has less interaction. To elucidate the concrete structure of these adsorbed species, isotopic analysis was performed.

In fig. 5 IR spectra of adsorbed C_2H_6 and CH_2DCH_2D are shown for the more stable species (a) and weakly adsorbed species (b). For the species (a), the same spectrum as that for CH_2DCH_2D was observed from adsorption of CH_3CH_2D. Based on the fact that two CD stretching bands appeared for both

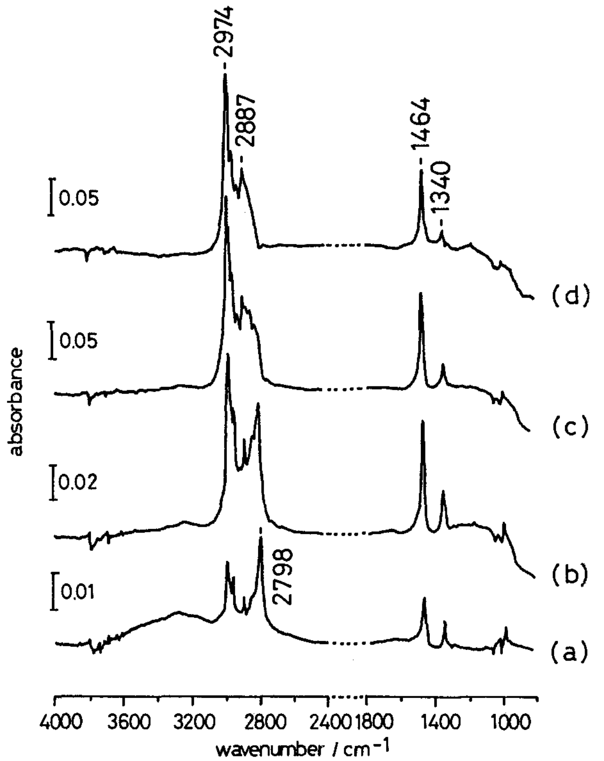


Fig. 4. IR spectra of adsorbed C_2H_6 at various temperatures: (a) 193 K; (b) 158 K; (c) 138 K and (d) spectrum of (c)–(a).

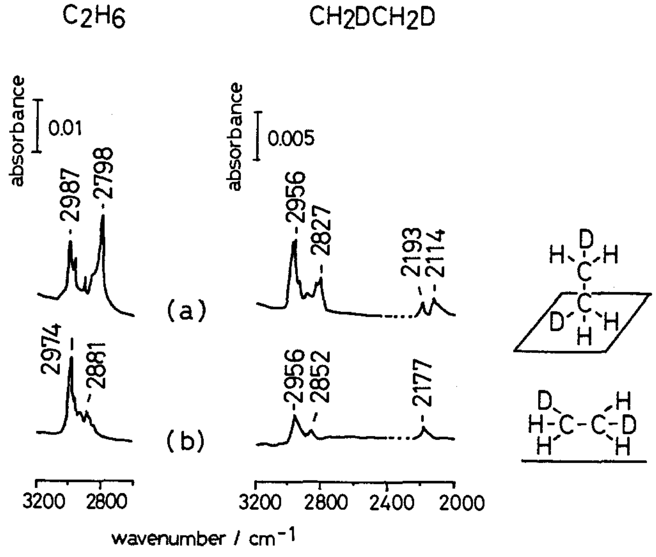


Fig. 5. IR spectra of adsorbed ethane; (a) end-on ethane and (b) side-on ethane, both for CH_3CH_3 and CH_2DCH_2D.

CH_2DCH_2D and CH_3CH_2D, the adsorption structure of (a) is regarded as "end-on" form as illustrated on the right hand of the spectra; ethane is adsorbed on ZrO_2 with one methyl group interacting with the surface. This type of adsorption causes the shift of the CH(CD) stretching band to low frequency as a result of interaction of methyl group with the surface. On the other hand, only one CD stretching band was observed for CH_2DCH_2D adsorption in (b) with a shoulder band. Therefore it is expected that ethane is weakly adsorbed in terms of "side-on" ethane as the illustration, where its two methyl groups are equivalent to the surface [28]. The same conclusion was obtained by the comparison of spectra for adsorbed CD_3CD_3, CD_3CHD_2 and CHD_2CHD_2.

4. REACTION OF ZrH(a) AND C_2H_4(g)

The metal-H species derived from the heterolytic dissociative adsorption has been regarded as an active intermediate for hydrogenation over metal oxides because of high activity of metal catalysts for hydrogenation via metal-H species. For example ZnH and OH are regarded as the reaction intermediate for ethene hydrogenation over ZnO. Based on this background, ethene was added to the ZrO_2 surface where ZrH and OH were preadsorbed.

400 Torr of H_2 was introduced to the IR cell at room temperature followed by cooling in the atmosphere of H_2 gas. Following this, the gas phase was evacuated at 223 K at which ZrH species stably exists without gas phase [26]. C_2H_4 was diluted by He in order to lower the pressure of C_2H_4 and was added to ZrO_2 with ZrH at 223 K. In fig. 6, the relative amount of adsorbed ZrH, s-π-bonded and π-bonded ethene are plotted versus the experimental proce-

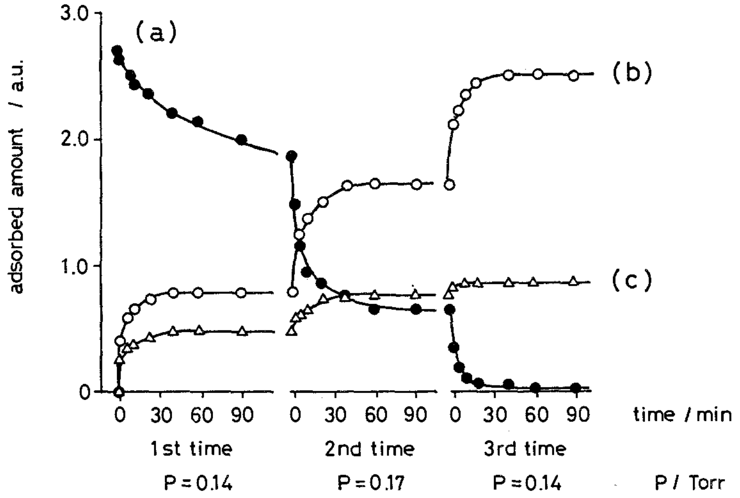


Fig. 6. Time course of the adsorbed species during the reaction, ZrH(a) and OH(a)+C_2H_4(g); (a) ZrH species (1562 cm^{-1}), π-bonded ethene (1338 and 1446 cm^{-1}) and s-π-bonded ethene (1338 cm^{-1}).

dure by use of the bands at 1562, 1338; and 1338 and 1446 cm^{-1}, respectively. The intensity of OH species could not be measured because of its weak absorption band. At each time, ethene was added at the pressure of 0.14 or 0.17 Torr and the following addition was performed after the complete adsorption of former one. The adsorption curves in fig. 6, as well as the spectra of both s-π- and π-bonded ethene observed during the experiment in fig. 6, were exactly the same as those observed when ethene was adsorbed on ZrO_2 without hydrogen species under the same condition. In addition, no band other than ZrH and ethene was observed. This result suggests that the ZrH species did not react with ethene provided from gas phase but was only removed by ethene adsorption on the site, which is quite different from the result of Kokes and co-workers on ZnO [22]. They observed the newly produced species during the reaction over ZnO in the presence of ZnH and OH bands and assigned to the species surface bonded ethyl. This observation led them to conclude that the ZnH and OH were the intermediate for ethene hydrogenation, while ZrH and OH are not over ZrO_2.

5. REACTION OF ADSORBED ETHENE AND H_2

5.1. $C_2H_4(a) + H_2(g)$

Adsorbed ethene was hydrogenated at 183 K with 100 Torr of H_2, and the transformation of the spectra was observed as shown in fig. 7. Within 2 hr at the initial stage, new bands at 2974, 2862 and at a shoulder of the band at 1446 cm^{-1} were observed (fig. 7(b)). These are attributed to the newly produced species. However, at the final stage of the reaction when ethene was almost consumed, another species with the bands at 2985, 2886 and 1464 cm^{-1} was observed (fig. 7(d)). This species is considered to be the final product, i.e., stably adsorbed ethane because no distinct change in the spectra was observed after 9 hr of the reaction.

5.2. $C_2H_4(a) + D_2(g)$

Spectra during the $C_2H_4(a) + D_2(g)$ reaction were observed in order to compare the reaction products and the adsorbed ethane in addition to those observed during the $C_2H_4(a) + H_2(g)$ reaction. Both spectra in fig. 8 are described in the ratio spectra which show the change of the spectra. Therefore, decreased bands are observed as reverse peaks and the bands observed upward are due to the species produced during the reaction. The spectrum in fig. 8 (a) shows the spectrum of the change in the first two hours, and that of the final stage of the reaction is presented in fig. 8 (b). Only CH_2DCH_2D was produced during the $C_2H_4(a) + D_2(g)$ reaction at 193 K. This was confirmed by the NMR analysis of the product. When the spectra of adsorbed ethane (figs. 4 and 5) and those taken during the reaction (figs. 7 and 8) are compared, it is clear that side-on ethane is initially produced during ethene hydrogenation and transforms

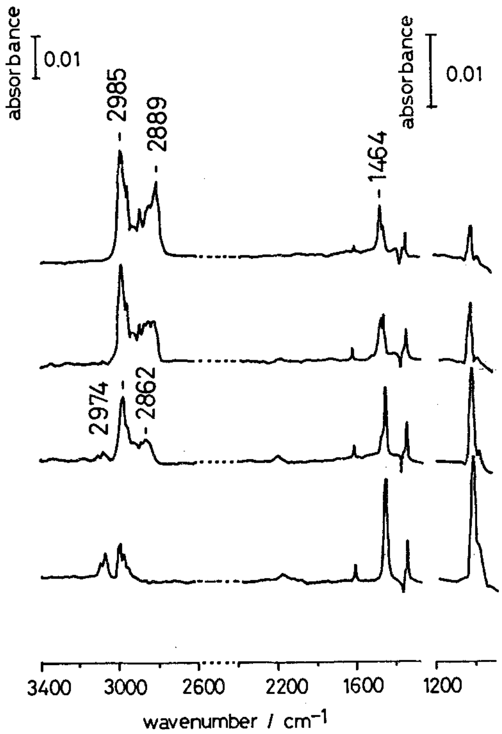


Fig. 7. IR spectra taken during the reaction, $C_2H_4(a)+H_2(g)$ at 183 K: (a) before introduction of H_2; (b) 2 hr of the reaction; (c) 6 hr and (d) 9 hr.

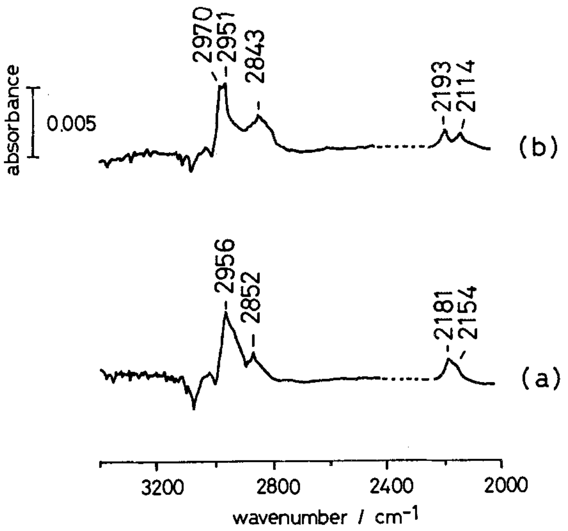
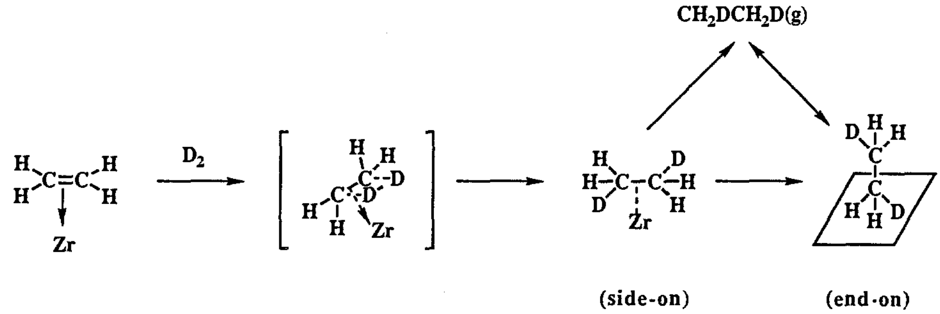


Fig. 8. Ratio spectra of the reaction, $C_2H_4(a)+D_2(g)$ at 193 K; (a) [1 hr of the reaction]/[before introduction of D_2] and (b) [4 hr of the reaction]/[3 hr of the reaction].



Scheme 1.

to the more stable end-on one. The IR spectra taken during the comparable reaction, $C_2D_4(a) + H_2(g)$, resulted in the same spectra of side-on CHD_2CHD_2 followed by end-on CHD_2CHD_2.

5.3. The total reaction mechanism

The total mechanism of ethene hydrogenation over ZrO_2, especially where and how hydrogen is activated is considered. ZrH and OH species were not thought to react with ethene. However the possibility of the other species derived from hydrogen adsorption must be considered. The sites for hydrogen adsorption are completely obstructed by surface OH produced by H_2O adsorption [26]. However, ethene hydrogenation occurred on the OH modified surface and the same spectra as those in fig. 7 were observed, although the adsorbed amount was much less [27]. This means that adsorbed hydrogen species due to hydrogen adsorption on bare ZrO_2 are not the reaction intermediate.

The mechanism concluded by IR observation is proposed in Scheme 1. In this scheme a hydrogen molecule is activated on zirconium which is induced by ethene adsorption. Following this, it is involved in the activated complex. Therefore, side-on ethane maintaining the conformation of the activated complex is produced at first and transforms to the more stable end-on ethane or desorbs from the surface. This speculation is supported by the experimental fact that above 183 K where the reaction was observed side-on ethane was not dominantly produced from ethane adsorption (fig. 4). The scheme appears to be the most probably mechanism, although the activated complex could not be observed. However, the process of hydrogen insertion can explain the suggestion made by a kinetic study of Sinfelt [17,18] that hydrogen would be supplied directly from the gas phase during the ethene hydrogenation over Al_2O_3.

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