In-situ characterisation of the surface intermediates for the ethanol dehydration reaction over γ-alumina under dynamic conditions

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Abstract

The dynamic behavior of the ethanol adsorption on γ-alumina were investigated at 180 and 200°C by the transient-response method coupled with FT–IR data of the catalyst surface. The existence of three adsorbates was demonstrated: a reacting species which is the precursor for the formation of the gas-phase ethene; an inhibiting species responsible for the low steady-state reaction rate; and a spectator species accumulating on the catalyst surface. Their infrared spectra indicate an ethoxide-like structure for the three adsorbates. Their C–H stretching bands can be depicted by four Lorentzians whose parameters indicate different surface environments. The surface concentration of the reacting species was determined on the basis of the transient ethene response. A value of 0.77±0.07 mol/kg\textsubscript{cat} was found at 180°C. The surface concentration of the spectator species was determined by ex-situ thermogravimetric experiments. A value of 0.13±0.01 mol/kg\textsubscript{cat} was found at 180°C. The most likely structure of this species corresponded to an ethanol molecule coordinated in a bidentate manner on Al\textsuperscript{3+} cations, with stabilisation of the alcoholic-hydroxyl group via lateral hydrogen bonding with an adjacent surface hydroxyl. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Ethanol dehydration; FT–IR; Adsorbed species; Dynamic conditions

1. Introduction

The stop-effect, a dynamic phenomenon first described by Koubek et al. [1,2], is observed for the reactions of deamination and alcohol dehydration over amphoteric metal-oxide catalysts, such as alumina. It consists in a temporary increase of the reaction rate when the reactant feed is switched off and replaced by an inert gas stream with the total flow rate kept constant. This phenomenon was also observed by Makarova et al. [3] with the dehydration of n-butanol on H-ZSM-5 and amorphous aluminosilicate, and by Moravek and Kraus [4] with the ethanol dehydration on alumina.

Two basic models were discussed by Thullie and Renken [5,6] to describe the stop-effect. The first model considers the adsorption of the reactant on two different sites S\textsubscript{1} and S\textsubscript{2} with a consecutive reaction involving an adsorbed intermediate (on S\textsubscript{1}) and a free site, S\textsubscript{2}. The reactant A is only weakly adsorbed on the site S\textsubscript{2} and desorbs rapidly when the feed is switched off, increasing the number of free sites S\textsubscript{2} available for the reaction. Therefore, the stop-effect is provoked by an inhibiting effect of the...
reactant which is suppressed by its replacement by an inert gas. The second model considers the chemisorption of the reactant on a single site with a consecutive adsorption of the reactant on the first adsorbed layer. Again, the second layer is only weakly adsorbed and by switching off the reactant feed the concentration of the chemisorbed complex necessary for the reaction is increased. In that case, the stop-effect is explained by a blocking phenomenon occurring at steady-state due to the formation of a non-reactive complex.

It was previously shown with the dehydration of ethanol-to-ethene on γ-alumina [7] that the first model (Eqs. (1)–(3)), considering the existence of two types of sites, gives a better description of the stop-effect than the second model. This model was further simplified in order to decrease the number of parameters required for the modelling. The adsorption on S1 is considered to be irreversible (Eq. (1)), whereas it is weak on S2 (Eq. (2)). The exact physical nature of S1 and S2 is not completely clear. By comparison with the explanation proposed by Koubek et al. [1] for the stop-effect which is based on the mechanism for the amines elimination reactions on alumina, S1 can be associated with an acid site and S2 with a basic site.

The diethylether formation is described, for simplicity, by a quasi-homogeneous reaction term (Eq. (4)).

$$\begin{align*}
A + S_1 & \rightarrow k_1 AS_1 \quad A : \text{ethanol} \\
A + S_2 & \rightarrow k_2 AS_2 \quad E : \text{ethene} \\
AS_1 + S_2 & \rightarrow k_3 E + W + S_1 + S_2 \quad W : \text{water} \\
2A & \rightarrow D + W \quad D : \text{diethylether}
\end{align*}$$

The adsorbed intermediates, identified as surface-bound ethoxides, were monitored under dynamic conditions using in-situ infrared spectroscopy. Their similar structure produce similar infrared spectra with no characteristic band for either AS1 or AS2. These two species can only be distinguished by their different dynamic behaviour during the inert gas purge. The AS2 concentration decreases immediately, whereas AS1 is slowly consumed to form ethene. This different kinetic behaviour is responsible for the particular shape of the observed infrared signal.

In this work, we paid close attention to the dynamic behaviour of the different reaction adsorbates. Their nature and formation pathway are studied by the transient-response method coupled with in-situ infrared data of the catalyst surface. They were further characterised by the calculation of their spectral line shapes using non-linear least squares fitting of Lorentzians. Finally, thermogravimetric experiments are used to determine the surface concentration of the most stable species.

2. Experimental

The apparatus, catalyst and gases employed, as well as the infrared bands attribution, have been previously described in detail [7].

2.1. Apparatus

The flow-apparatus consisted of two feed sections converging to a four-way valve, a fixed-bed tubular reactor, an infrared transmission cell and a gas chromatograph. The fixed-bed reactor, used to achieve a sufficient ethanol conversion, was placed just in front of the infrared cell. RTD experiments showed that it behaves like a plug-flow reactor, and the infrared cell like a continuous stirred tank reactor. The tubular reactor was described by the tanks-in-series model using nine tanks for the catalyst compartment.

2.2. Gases and catalyst

The carrier gas was argon (>99.99%, Carbagas, Lausanne, Switzerland) and the ethanol (>99.8%, No. 02860, Fluka Chemie AG, Buchs, Switzerland) feed was provided by a temperature-controlled bubble column fed by argon.

As catalyst, γ-alumina (Type Al-3982, Engelhard De Meern B.V., De Meern, The Netherlands) was used in this study. The specific area and pore-size distribution were determined via Sorptomatic (Type 1900, Carlo Erba Instruments, Milano, Italy). The specific area is 163±2 m²/g and the average pore diameter 7.4±0.1 nm. The impurities present in the
catalyst are Fe$_2$O$_3$ (0.07%), SiO$_2$ (0.01%) and Na$_2$O (0.06%) [8].

A self-supporting wafer, 13 mm in diameter, was prepared by pressing alumina powder for the infrared transmission cell (7 × 10$^8$ N/m$^2$). Other wafers were pressed and then grinded to particles of 0.35–0.16 mm diameter for the fixed-bed reactor. A total of 483 mg of the catalyst were used in the reactor and a 27 mg wafer was placed in the cell.

2.3. Procedure

The stop-effect was measured at 180 and 200°C and a pressure of 140 kPa according to the following sequence: 108 min ethanol/830 min argon. The initial ethanol concentration was 0.25 mol/m$^3$ and the total flow rate was 200 ml (NTP)/min. Before each experiment, the catalyst was pre-treated at 415°C for 1 h under inert gas in order to remove the adsorbed ethoxide species. In addition, an infrared background spectrum was measured at the reaction temperature under inert gas. This procedure leads to a reproducible surface state for each measurement.

2.4. In-situ infrared spectra

Three types of strongly adsorbed species have been already identified [7]: surface hydroxyl groups, surface-bound ethoxides and surface acetate groups. The acetates are formed by the adsorption of ethanol when the catalyst is used for the first time. As they do not desorb during the catalyst pre-treatment, they remain on the surface throughout all the subsequent experiments. The ethoxides are thought to be the reaction intermediates, corresponding to AS$_1$ and AS$_2$ in the two sites model (Eqs. (1)–(3)). Their concentration is proportional to the calculated height of the 2970 cm$^{-1}$ absorbance band with a baseline correction between 3100 and 2600 cm$^{-1}$ [7]. This measurement technique gave similar results to those obtained by calculating the area under the C–H stretching bands. The measured ethoxides concentration corresponds to the sum of the concentrations of AS$_1$ and AS$_2$.

2.5. Thermogravimetric experiments

A STA 625 Rheometrics balance was used for the thermogravimetric analysis with a nitrogen flow of 140 ml (NTP)/min. The catalyst was placed in the balance immediately after the transient experiments. The mass loss and catalyst temperature were measured as a function of time. Approximately 40 mg of catalyst were used in each experiment.

3. Results and discussion

The behaviour of the infrared signal in a stop-effect experiment can be interpreted on the basis of the simultaneous gas phase and surface responses. The ethene concentration is measured at the outlet of the system fixed-bed/infrared cell, whereas the 2970 cm$^{-1}$ absorbance is determined in the cell. A typical example for a reaction temperature of 200°C is presented in Fig. 1, after an ethanol feeding time of 108 min. Three distinct kinetic phases (1, 2 and 3) are observed on the surface after the stop, corresponding...
to three different species: a rapid decrease, lasting \( \approx 5-10 \text{ min} \) (phase 1); followed by a slow diminution; and a plateau at the end of the transient. The first decrease is due to the desorption of the inhibiting species adsorbed on the basic sites and coincides with the simultaneous sharp increase of ethene formation. The second diminution (phase 2) results from the consumption of the reacting intermediates adsorbed on the acid sites to form ethene [7]. During this period, another rate enhancement is observed in the gas phase \( \approx 60 \text{ min} \) after the stop, which can be described by adding a new reaction step for the reacting species to the already developed model [9]. Due to the fact that the infrared signal is measured through the catalyst wafer, after the fixed bed, the sensitivity of the infrared signal is relatively low. Therefore, the surface behaviour does not reflect the second rate enhancement. The origin of the plateau (phase 3) cannot be explained directly: an adsorbate seems to be stuck on the surface when no more ethene is produced in the gas phase. The formation of this third species is probably also responsible for the increase of the infrared signal during the ethanol feeding, observed when the gas-phase signal is already stationary. A similar phenomenon of dissymmetry between the gas phase and surface behaviour was also observed under periodic operation of the system [7]: the periods invariance was obtained for the ethene after a different first cycle, whereas the infrared signal was not reproducible. Its value still increased during the next two periods before being stable. The existence of a slow parallel adsorption of ethanol under a non-reacting form was supposed to account for this difference in the dynamic behaviour of the gas phase and the surface.

A different experimental procedure was applied to study the influence of this third species which consisted of stopping the reactant feed before a stable surface signal was obtained. The Fig. 2 shows the transient responses after feeding times of 18, 36 and 108 min for a reaction temperature of 180°C. The temperature influence on the ethene and infrared transients is important. Approximately 200 min after the stop, no more ethene is produced at 200°C, Fig. 1, whereas it is still detected 800 min after stopping the ethanol feed at 180°C, Fig. 2. From simulated curves [10], an activation energy of ca. 100 kJ/mol was estimated for the surface reaction step (Eq. (3)).

The intensity of the 2970 cm\(^{-1}\) absorption band obtained before stopping the feed decreases in parallel with the ethanol exposition time due to the surface unsaturation. During the inert purge, the three infrared signals decrease regularly without intersecting each other. In fact, the difference between the three curves remains constant throughout all the transient. The absorbance increase compared to the 18 min ethanol feeding experiment is 0.04 for 36 min feeding and 0.07 for 108 min. Comparatively, the simultaneous gas-phase responses are unaffected by the variation of the feeding time: the same amount of ethene is produced at steady-state, and the transient responses after the stop are identical. As there is no relationship between the ethanol accumulation on the surface and the gas-phase products formation, it can be postulated that ethanol accumulates on \( \gamma \)-alumina under the form of a non-reacting species. It is formed by the direct adsorption of ethanol on the catalyst, as the migration
or transformation of adsorbed ethanol would have implied the same infrared absorbance at the end of all the transients. This supposition was further confirmed by carrying out two consecutive experiments (not shown here) with a feeding time of 36 min, without catalyst pre-treatment in-between. The resulting infrared signal is located between the ones observed for the 36 and 108 min feeding experiments, corresponding to an effective time of 72 min under ethanol.

Hence, the presence of three different species on the catalyst surface can be assumed. The fact that they exhibit a completely different dynamic behaviour can be advantageously used to determine their own infrared spectra. In Fig. 3, the infrared spectra at steady-state (spectrum (a)), after 12 min of inert gas purge (spectrum (b)), and at the end of the transient (spectrum (c)) are presented. At steady-state all the adsorbates are present, whereas the inhibiting species is completely desorbed after 12 min under inert conditions, and only the spectator species remains on the surface at the end of the transient. On each spectrum, a continuous absorption is observed over the entire accessible spectral range. It has already been reported by Knözinger and Stübner [11] and Travert et al. [12], who explained it as the consequence of very easily polarizable hydrogen-bond formation. The bands attribution, Table 1, was made by analogy with the gas-phase spectrum, and by comparison with previous works dealing with alcohols adsorption on metal-oxide catalysts. The O–H group vibration at 3725 cm\(^{-1}\) belongs to a \(\gamma\)-alumina hydroxyl group,

![Figure 3](image.png)

**Fig. 3.** In-situ infrared spectra of the catalyst surface. Spectrum (a) steady-state; (b) 12 min after the stop; (c) end of the transient. \((T_R=200^\circ C, \ C_{A,0}=0.25 \text{ mol/m}^3, \ Q=200 \text{ ml (NTP)/min}).\)

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**Table 1**

Infrared bands attribution for adsorbed ethanol on \(\gamma\)-alumina

<table>
<thead>
<tr>
<th>Wave number (cm(^{-1}))</th>
<th>Vibration</th>
<th>Reference</th>
<th>Wave number (cm(^{-1}))</th>
<th>Vibration</th>
<th>Reference</th>
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<tr>
<td>2970</td>
<td>(\nu_\text{(CH}_3\text{)})</td>
<td>[11,15,16]</td>
<td>1390</td>
<td>(\delta_\text{(CH}_3\text{)})</td>
<td>[11–13,15]</td>
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<tr>
<td>2930</td>
<td>(\nu_\text{(CH}_2\text{)})</td>
<td>[11,15,16]</td>
<td>1170</td>
<td>(\nu(\text{CO}), \nu(\text{CC}))</td>
<td>[12,15]</td>
</tr>
<tr>
<td>2900</td>
<td>(\nu_\text{(CH}_2\text{)})</td>
<td>[16]</td>
<td>1115</td>
<td>(\nu(\text{CO}), \nu(\text{CC}))</td>
<td>[12,15]</td>
</tr>
<tr>
<td>2870</td>
<td>(\nu_\text{(CH}_3\text{)})</td>
<td>[11,15,16]</td>
<td>1070</td>
<td>(\nu(\text{CO}), \nu(\text{CC}))</td>
<td>[12,15]</td>
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whereas the two bands ca. 3500 cm\(^{-1}\) belong to stabilised alcoholic-hydroxyl group \([11,13]\). The two bands at 1480 and 1560 cm\(^{-1}\) are those of an acetate structure. Their peculiar appearance is due to the presence of this species in the background spectrum. All the other vibrations are attributed to an ethoxide species, generally thought to be the reaction intermediate. Chemisorbed water formation, with a bending vibration ca. 1630 cm\(^{-1}\) \([15]\), is not observed.

The general shapes of the spectra are the same and only slight differences in the relative intensities of the various vibrations are noticed. Therefore, it can be stated that the three species have an ethoxide-like structure. The surface hydroxyl groups are completely restored at the end of the transient, except for the 3720 cm\(^{-1}\) band which is still present. The stabilised alcoholic-hydroxyls groups ca. 3550 cm\(^{-1}\) do not diminish to the same degree as the other bands. Hence, it can be stated that the spectator species possesses a stabilised alcoholic-hydroxyl group and interacts with a surface hydroxyl group. Knözinger and Stübner \([11]\) postulated an adsorption structure for the most strongly held alcohol consistent with the above observations. The oxygen atom of the alcohol molecule is coordinated in a bidentate manner to Al\(^{3+}\) cations and the alcoholic-hydroxyl group is hydrogen bonded to a surface hydroxyl. This is the most likely structure of the spectator species.

The measured infrared spectra are linear combinations of those of the adsorbed species. Therefore, the real spectra of these adsorbates can be calculated by judiciously subtracting them from each other (Fig. 4). The spectrum of the spectator species (spectrum \((c)\)) is measured at the end of the transient when no more ethene is produced. The spectrum of the inhibiting species (spectrum \((\beta)\)) is obtained by subtracting the spectrum \((b)\) from the spectrum \((a)\), and this of the reacting species (spectrum \((\alpha)\)) by subtracting the spectrum \((c)\) from \((b)\). These calculations are made for the C–H stretching region, with a baseline correction between 3200 and 2600 cm\(^{-1}\) and an artificial shift to zero absorbance, in order to account for the previously described continuous absorption. The resulting spectra show important differences in the relative intensities and in the positions of their bands. In order to quantify these differences, curve-fitting calculations by the non-linear least squares method were carried out on these spectra. Lorentzian functions are chosen, as they represent the natural line shapes in infrared spectroscopy \([17]\). Each C–H stretching group can be fitted with four Lorentzians whose

![Fig. 4. C–H stretching bands of the infrared spectra. Spectrum (a) steady-state; (b) 12’ after the stop; (c) end of the transient; \(\alpha=\) (b)–(c); \(\beta=\) (a)–(b); \(T_R=200^\circ\text{C}; C_{A_0}=0.25\) mol/m\(^3\); \(Q=200\) ml (NTP)/min).](image-url)
Table 2
Parameters of the Lorentzians peak functions

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<tr>
<th>Species</th>
<th>Parameter</th>
<th>Peak 1</th>
<th>Peak 2</th>
<th>Peak 3</th>
<th>Peak 4</th>
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<td>Reacting</td>
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<td>2904</td>
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<td>0.076</td>
<td>0.036</td>
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<td>0.16</td>
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<td></td>
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<td>22</td>
<td>28</td>
<td>72</td>
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<tr>
<td>Inhibiting</td>
<td>Position (cm⁻¹)</td>
<td>2970</td>
<td>2927</td>
<td>2901</td>
<td>2871</td>
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<tr>
<td>(Spectrum b)</td>
<td>Height (°)</td>
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<td>0.011</td>
<td>0.077</td>
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<td></td>
<td>Relative height (°)</td>
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<td>0.11</td>
<td>0.77</td>
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<tr>
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<td>11</td>
<td>70</td>
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<tr>
<td>Spectator</td>
<td>Position (cm⁻¹)</td>
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<td>2935</td>
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<td>(Spectrum c)</td>
<td>Height (°)</td>
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<td>0.012</td>
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<td>0.34</td>
<td>0.17</td>
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<tr>
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<td>FWHH (cm⁻¹)</td>
<td>23</td>
<td>21</td>
<td>12</td>
<td>73</td>
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</table>

parameters are given in Table 2. Due to different surface environments and adsorption sites, the relative heights and the full width of the peaks at half height vary for the three ethoxide species. The 2970 cm⁻¹ peak is the highest and best described peak. Its position is similar for the reacting and the inhibiting species, but is shifted to higher values for the spectator species. Porchet [8] and Kiwi-Minsker et al. [18] have reported a similar shift of the C–H stretching vibration in the case of adsorbed methanol over selectively Mg²⁺-modified γ-alumina which could be correlated to the strength of adsorption. Assuming this would indicate a stronger adsorption of the spectator species in comparison to the other two. A concomitant switch of the other CH₃ stretching vibration (Peak 4, Table 2) to higher values is also observed.

The calculated spectra can be added together to simulate the expected experimental spectrum. An excellent agreement is achieved with the measured spectrum (see Fig. 5). This shows that the spectra of

![Fig. 5. Comparison between measured and calculated spectra. Solid lines: experimental spectra; dashed lines: calculated spectra. Spectrum a: reacting species; b: inhibiting species; c: spectator species. (TR=200°C, CA₀=0.25 mol/m³, Q=200 ml (NTP)/min).](image)
the adsorbed species can be well described with four Lorentzians.

The surface concentrations of the reacting and the spectator species can also be determined on the basis of their dynamic behaviour. As it was shown in the Section 1, the adsorption of the reacting species is considered to be irreversible (Eq. (1)). Therefore, its consumption is only due to the ethene formation. By integrating the complete ethene molar flow after stopping the ethanol feed, the number of ethene moles produced during the stop-effect is obtained, which is equal to the number of moles of the reacting species. Hence, the surface concentration of this species is calculated by dividing the integrated molar flow by the total catalyst mass in the system. A value of $0.77 \pm 0.07 \text{ mol/kg}_{\text{cat}}$ is found at $180^\circ \text{C}$, which corresponds to the surface concentration of site 1, assuming a complete steady-state surface coverage at this temperature. Considering that the cross-sectional area of the ethanol molecule adsorbed on a solid surface is $28.3 \text{ Å}^2$ [19], this represents ca. 80% of a monolayer. At $200^\circ \text{C}$ the integration leads to a value of $0.69 \pm 0.09 \text{ mol/kg}_{\text{cat}}$, reflecting the decrease of the surface coverage with the reaction temperature.

In the background spectrum of the catalyst (Fig. 6) only surface hydroxyl groups, with vibrations between $3450$ and $3800 \text{ cm}^{-1}$, and surface-bound acetates, with two peaks at $1480$ and $1560 \text{ cm}^{-1}$, are present. As no C–H stretching vibrations ca. $2900$–$3000 \text{ cm}^{-1}$ are detected, it is concluded that the spectator species is removed during the catalyst pre-treatment. Consequently, it can be postulated that this species is stable at the reaction temperature but can be removed at higher temperatures. Thermogravimetric experiments were made with the freshly used catalyst (Fig. 7). The stability of the spectator species at low temperature is sufficient to ensure reproducible measurements. The catalyst was first heated at $180^\circ \text{C}$ for 1 h to remove water, and then its temperature was raised to $415^\circ \text{C}$ with an heating rate of $10^\circ \text{C/min}$. This temperature was maintained for another hour to desorb completely the spectator species. This cycle was repeated a second time to ensure a complete desorption. The mass loss is calculated by the mass difference measured at $180^\circ \text{C}$ before and after the $415^\circ \text{C}$ heating phase. The further mass decrease observed at $415^\circ \text{C}$ is only due to the transient behaviour of the thermal analyser [20]. The measured weight of the probe is the difference between its real weight and other forces, such as the Archimedes force and the drag forces. A temperature increase causes an augmentation of the drag forces and a decrease of the Archimedes force, the result of which is a decrease of the apparent probe weight. Therefore, the mass decrease due to the desorption of the inhibiting species must be calculated at an identical catalyst temperature of $180^\circ \text{C}$. A sur-

Fig. 6. Background spectrum of the catalyst surface at $T=200^\circ \text{C}$ under inert gas.
face concentration of \(0.13 \pm 0.01\) mol/kg\(_{\text{cat}}\) is found at 180°C.

4. Conclusions

By applying simultaneous measurements of the gas phase and of the catalyst surface for the ethanol dehydration on \(\gamma\)-alumina, the existence of three adsorbed species with an ethoxide-like structure was demonstrated. These species are:

- a reacting species which is a precursor for the ethene formation;
- an inhibiting species which desorbs immediately under inert gas; and
- a spectator species which accumulates slowly on the catalyst surface during the ethanol feeding.

This last species is stable under inert gas up to 200°C, but can be removed at temperatures higher than 400°C. As it absorbs in the same infrared region that the reaction intermediates postulated in the two sites model, its formation must be taken into account when dealing with the modelling of the surface behaviour during the stop-effect. The simplest way is to subtract an offset corresponding to the absorbance measured at the end of the transient from all the infrared data.

5. Nomenclature

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<tr>
<th>Symbol</th>
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<tr>
<td>A</td>
<td>Ethanol</td>
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<tr>
<td>D</td>
<td>Diethylether</td>
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<tr>
<td>E</td>
<td>Ethene</td>
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<tr>
<td>FWHH</td>
<td>Full width at half height</td>
</tr>
<tr>
<td>FT–IR</td>
<td>Fourier Transform infrared spectroscopy</td>
</tr>
<tr>
<td>NTP</td>
<td>Normal conditions of temperature and pressure (0°C, 1.013 (\times 10^5) Pa)</td>
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<tr>
<td>S</td>
<td>Catalytic site</td>
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<tr>
<td>(T_R)</td>
<td>Reaction temperature</td>
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<td>W</td>
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5.1. Greek letters

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<td>(\delta)</td>
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5.2. Subscripts

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Acknowledgements

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References