# On the Mechanism of Catalytic Oxidation of CH₂Cl₂ on γ-Al₂O₃ and its Oscillatory Behaviour

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*Dedicated to Gerhard Ertl on the occasion of his 60th birthday*

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Adsorption of $CH_2Cl_2$ and its oxidation with dioxygen have been investigated on pure $\gamma$-$Al_2O_3$ by means of infrared spectroscopy and gas chromatographic analysis. Infrared spectroscopy showed that $CH_2Cl_2$ may be adsorbed on the alumina surface through chlorine ions either on two adjacent exposed Al ions at the (111) plane of $Al_2O_3$, or on the isoloated Lewis acid sites. The oxidation of $CH_2Cl_2$ at temperatures below 450°C yields an intermediate product $CH_3Cl$ with 50% of selectivity whereas the other half of the $CH_2Cl_2$ amount is totally oxidized to $CO_2$ and HCl. At temperatures higher than 450°C practically total conversion of $CH_2Cl_2$ to $CO_2$ and HCl takes place. Selfsustained oscillations of the $CH_2Cl_2$ conversion in a broad range are observed when water vapour is added to the feed. The mechanism explaining the nature of the activity of alumina in the $CH_2Cl_2$ oxidation and selectivity to $CH_3Cl$ as well as a possible reason of oscillations of the conversion are proposed.

Adsorption von $CH_2Cl_2$ und seine Oxydation mit Sauerstoff auf reinem $\gamma$-$Al_2O_3$ als Katalysator wurden mit IR Spektroskopie und gaschromatografischer Analyse untersucht. Analyse der „in situ"-IR-Spektren zeigte, daß $CH_2Cl_2$ auf der Oberfläche des $Al_2O_3$ durch Chlor-Atome entweder auf zwei auf die (111) Kristallfläche des $Al_2O_3$ nebeneinander liegenden exponierten Al-Ionen, oder auf den isolierten Lewissäure-Zentren, adsorbiert werden kann. Die Oxydation von $CH_2Cl_2$ bei Temperaturen unter 450°C gibt ein Zwischenprodukt $CH_3Cl$ mit 50% Selektivität, während die zweite Hälfte von $CH_2Cl_2$ zu $CO_2$ und HCl volloxidiert wurde. Bei Temperaturen über 450°C findet praktisch eine volle Umwandlung von $CH_2Cl_2$ zu $CO_2$ und HCl statt. Wenn Wasserdampf in den Reaktionsgemischstrom eingeführt wurde, sind selbsttreibende Oszillationen von $CH_2Cl_2$-Konversion im breiten Bereich zu beobachten. Der Mechanismus zur Erklärung der Natur von $Al_2O_3$ Aktivität in $CH_2Cl_2$ Oxydation und Selektivität zu $CH_3Cl$, sowie die möglichen Ursachen von Oszillationen der $CH_2Cl_2$-Umwandlung wurden diskutiert.

# 1. Introduction

Removal of halogenated hydrocarbons from flue-gases by catalytic oxidation is recently receiving more and more attention because of its growing importance in pollution control [1]. The main requirement is total conversion of chlorine contained in the organic molecule, into HCl, and oxidation of the organic part into $CO_2$ and $H_2O$ [2−5]. Whereas the mechanism of the combustion of a hydrocarbon molecule is partially understood, little is known about the mechanism of the cleavage of C−Cl bond and the formation of HCl. Both metals and transition metal oxides have been tried as catalysts [2−6], and recently considerable attention is paid to classical acid catalysts such as $Al_2O_3$, $TiO_2$, $SiO_2$ and their mixtures [7−9]. Some researchers claim the importance of acid sites, other emphasize that other parameters of the solid may be more important [4, 8]. It seemed therefore of interest to undertake a more detailed study of the mechanism of oxidation of chlorinated hydrocarbons using $Al_2O_3$ as catalyst, although it has been found not to be the best catalyst, because it contains well defined acid sites of Lewis type and its surface properties may be easily characterized by spectroscopic techniques [11]. Destruction of $CH_2Cl_2$ was selected as the model reaction as the H:Cl ratio enables the total conversion of Cl into HCl without the presence of other reagents.

# 2. Experimental

## 2.1 Materials

Alumina was prepared by hydrolysis of aluminum isopropoxide dissolved in isopropanol. Resulting precipitate was dried at 120°C for 2 hrs and then calcined at 550°C for 24 hrs.

## 2.2 Methods

X-ray diffraction (XRD) patterns were obtained with a DRON-3.0 diffractometer using Ni-filtered Cu $K_\alpha$ radiation. It has been found that the XRD pattern of alumina was characteristic of $\gamma$-$Al_2O_3$.

The BET surface area was determined from nitrogen adsorption at 77 K. The specific surface area of the sample was 210 m²/g.

Catalytic activity was measured in a conventional flow apparatus equipped with a glass reactor of inner diameter 10 mm. The volume of catalytic bed was 5 ml. The oxidation of methylene chloride was studied at different temperatures in order to determine light-off curves. Some experiments were done after a certain time-on-stream at 250°C and 300°C. Before each catalytic experiment samples were standarized at 450°C for 1 h.

Methylene chloride was introduced into the hot stream of air in order to allow its rapid evaporation. The concentration of methylene chloride in air was 2.5 g/Nm$^3$ of air. G.H.S.V. was 10,000 h$^{-1}$. Some experiments were done using air saturated with water vapour (24 Tr) at 25 °C.

Methyl chloride ($CH_3Cl$), $CO_2$, and HCl were the only products of the methylene chloride oxidation. $CH_3Cl$ and $CH_2Cl_2$ were analyzed by an "on-line" gas chromatograph (SRI 86 10A) with DCQF-1 column. HCl was absorbed in water by passing a given volume of the reaction gas. The amount of HCl was determined from the conductivity of HCl solution.

FTIR spectra were acquired in the transmition mode at room temperature by using a Nicolet 800 spectrometer. The resolution was 2 cm$^{-1}$. A thin alumina pellet (12 mg/cm$^2$) was used.

Before adsorption of pyridine (Fluka AG) alumina was outgassed at room temperature for 0.5 h followed by heating up (5°/min) to 450 °C under pressure 10$^{-6}$ Tr. Alumina pellet was activated at 450 °C for 1 h and then cooled to room temperature. Adsorption of pyridine (several Torr) was carried out for 15 min. Excess pyridine was evacuated for 1 h and FTIR spectrum was registered. Alumina pellet was then heated up (10°/min) to 150 °C, 250 °C, 350 °C or 450 °C and kept at each temperature for 1 h under continuous evacuation. From each temperature alumina pellet was cooled to room temperature for acquiring FTIR spectra.

$CH_2Cl_2$ was adsorbed on alumina pellet activated, as described above, from a stream of dry air containing 10 g of $CH_2Cl_2$/Nm$^3$ at 250 °C for 0.5 h. The sample was then cooled to room temperature in air and outgassed under pressure 10$^{-5}$ Tr. Alumina pretreated in such way was exposed to pyridine. The spectra of adsorbed pyridine were registered as described above.

$CH_2Cl_2$, in presence of water vapour (24 Tr), was adsorbed on standardized alumina pellets at 250 °C for 0.5 h. Then, the sample was cooled to 150 °C in moist air and evacuated under pressure 10$^{-5}$ Tr. Pyridine was adsorbed at 150 °C followed by desorption at 150 °C, 250 °C, 350 °C or 450 °C. FTIR spectra were registered, after cooling the pellet to room temperature from each temperature.

## 3. Results and discussion

The dependence of the initial and steady-state activities of alumina in oxidation of $CH_2Cl_2$ as a function of the reaction temperature is shown in Fig. 1. It can be seen that alumina deactivates strongly reaching, however, stable activity after a certain time-on-stream. The degree of deactivation depends on temperature. At high temperature alumina exhibits stable activity.

Steady-state activity of alumina together with selectivity to $CH_3Cl$ and HCl as a function of the reaction temperature is shown in Fig. 2. $CH_3Cl$ and
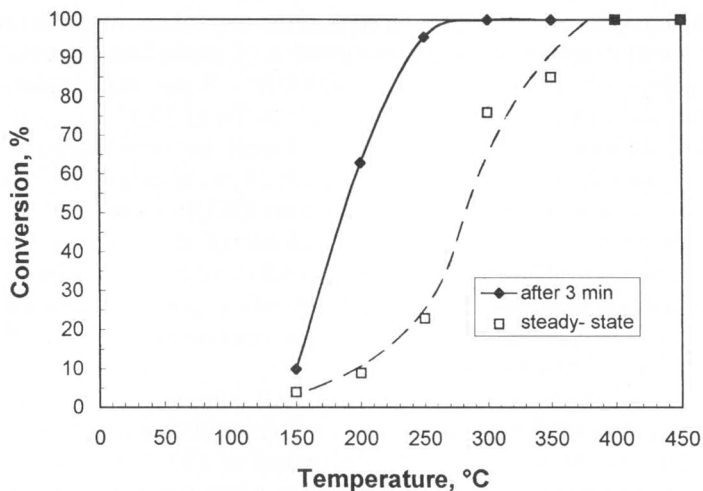
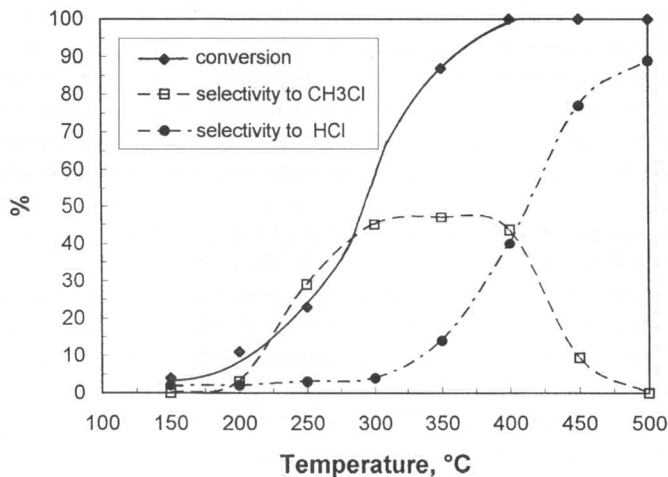**Fig. 1.** $CH_2Cl_2$ conversion as a function of temperature for undoped alumina.



**Fig. 2.** $CH_2Cl_2$ conversion and selectivity to $CH_3Cl$ and HCl in the steady state as a function of temperature. Undoped alumina.

HCl are the only chlorine-containing reaction products. $Cl_2$ is not detected. It follows from Fig. 2 that most of HCl remains adsorbed on alumina surface at the temperatures lower than 350°C. All HCl produced in the reaction is desorbed from the surface at the temperature 400°C. At the same time the selectivity to $CH_3Cl$ decreases abruptly.
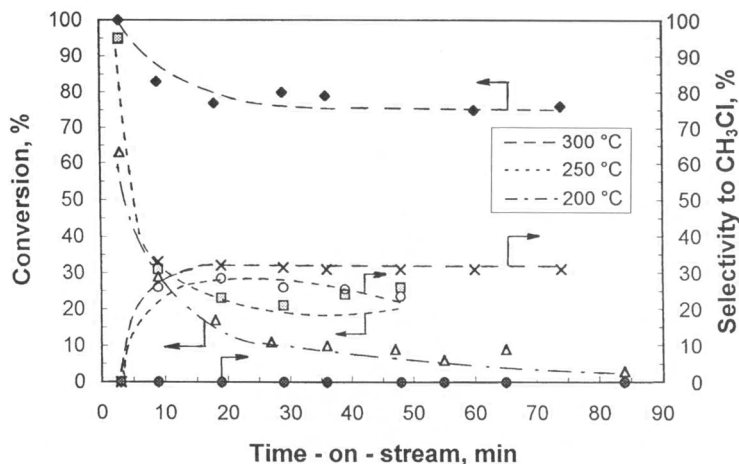
**Fig. 3.** The variation of $CH_2Cl_2$ conversion and selectivity to $CH_3Cl$ as a function of time-on-stream at different temperatures. Undoped alumina.

The dependence of the alumina activity and selectivity to $CH_3Cl$ on the time-on-stream at different temperatures is shown in Fig. 3. It can be seen that the initial activity is high at all temperatures. However, it decreases strongly at 200 and 250°C. $CH_3Cl$ is not observed in the reaction products at the very beginning of the reaction at 250°C and 300°C but it appears with time-on-stream in these temperatures. HCl is produced with poor selectivity (Fig. 2).

Fig. 4 presents the variation of the activity, selectivity to $CH_3Cl$ and yield of $CH_3Cl$ on the time-on-stream for alumina at 250°C in the presence of water vapour in the feed. It can be seen that the alumina activity, after initial decrease, begins to oscillate and so does selectivity to $CH_3Cl$. Yield of $CH_3Cl$ after decrease at the beginning of the reaction, remains stable. HCl is not observed in products.

X-ray analysis shows that $Al_2O_3$ obtained in our experiments has the structure of defected spinel $\gamma$-$Al_2O_3$. After dehydroxylation at 450°C for 1 h under the pressure of $10^{-6}$ Torr 5 different kinds of OH groups were formed at the surface as indicated by the IR spectra shown in Fig. 5. Two of them, with stretching frequencies 3682 $cm^{-1}$ and 3731 $cm^{-1}$, prevail, other three are visible as shoulders at 3755 $cm^{-1}$, 3772 $cm^{-1}$ and 3790 $cm^{-1}$. Some of the surface OH groups are hydrogen-bonded, as indicated by the presence of a broad band with maximum at about 3570 $cm^{-1}$. These results are in a very good agreement with the spectra of $\gamma$-$Al_2O_3$ quoted by Saad *et al.* [12].

Recent studies of the structure of aluminas, obtained by oxidation of very pure aluminium in an argon-oxygen mixture, carried out with the help of HREM, showed that small particles of $\gamma$-alumina have almost spherical
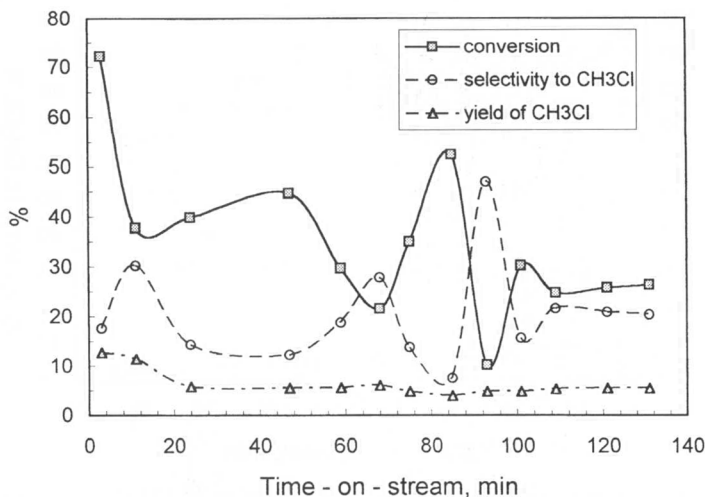
**Fig. 4.** The variation of $CH_2Cl_2$ conversion, selectivity to $CH_3Cl$ and yield of $CH_3Cl$ as a function of time-on-stream at 250°C in the presence of water vapour in the feed (24 Torr).
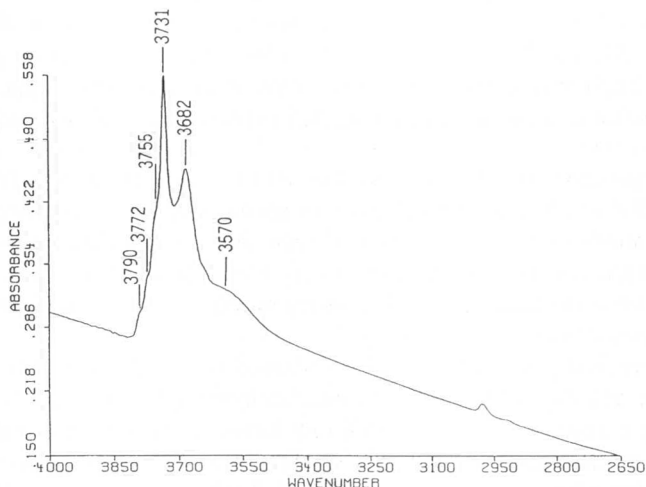


**Fig. 5.** IR spectra of $Al_2O_3$ activated at 450°C for 1 h under vacuum of $10^{-6}$ Torr.

shape and the exposed crystal planes are facetted so that predominant surfaces are of the (111) type, on which oxygen atoms are hexagonally arranged [13]. Also the (110) planes found previously to be preferentially exposed in the case of $\gamma$-alumina [11] consist of many small (111) facetts.
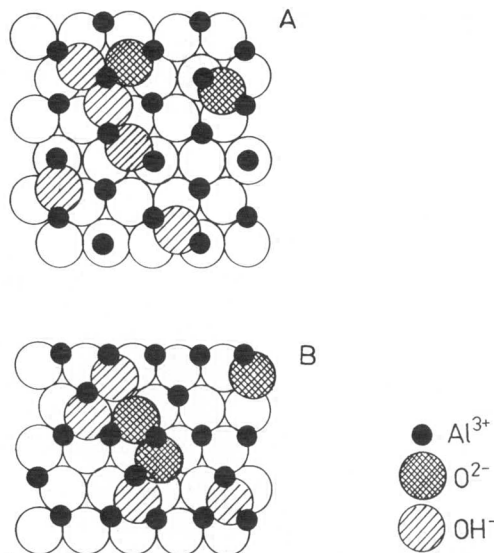
**Fig. 6.** A) (111)-face of alumina spinel lattice, A-layer; B) (111)-face of alumina spinel lattice, B-layer.

Comparison of the frequencies of OH groups observed here with those summarized by Knözinger [11] shows that dehydroxylation of our preparation left at the surface mainly OH groups located in the centre of three exposed octahedrally coordinated Al ions (type III in Knözinger's notation, 3682 cm$^{-1}$) and OH groups located between exposed octahedrally and tetrahedrally coordinated Al ions (type IIa, 3731 cm$^{-1}$). Other types of OH groups are present in small quantities only. A model of the Al$_2$O$_3$ surface, studied in our experiments, may be thus proposed as shown in Fig. 6.

On exposure to pyridine vapour the intensity of the band at 3682 cm$^{-1}$ remains practically unchanged. This is clearly visible from Fig. 7A, in which difference spectra are illustrated, registered after adsorption of pyridine at room temperature and its desorption at different temperatures. It may be seen that pyridine interacts with all OH groups present at the surface except those responsible for the band at 3680 cm$^{-1}$, forming H bonds through its aromatic electron system, as indicated by the appearance of the broad band with maximum at 3560 cm$^{-1}$. This is consistent with the results illustrated in Fig. 7A and B which show the absence of the bands of pyridinium ions and the presence of the bands of pyridine coordinatively bound to Lewis sites formed by exposed Al ions. It may be noticed that two types of Lewis acid sites are present, characterized by doublets of coordinatively bound pyridine at 1450/1456 and 1617/1623 cm$^{-1}$ [12].
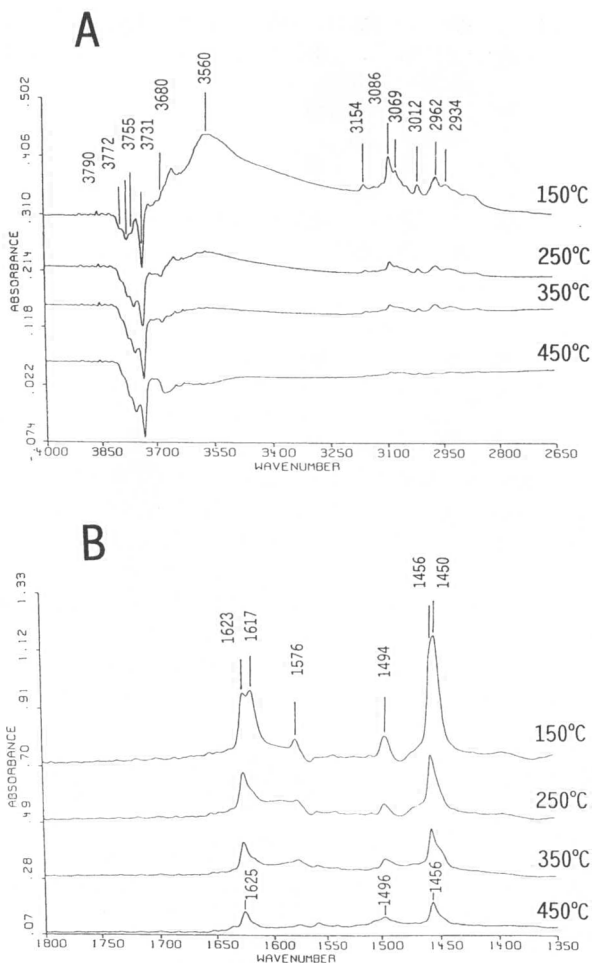
**Fig. 7.** The difference IR spectra of $Al_2O_3$ after adsorption of pyridine at room temperature and its desorption at different temperatures. The spectrum of $Al_2O_3$ registered before the experiment has been subtracted. A) stretching vibration range, B) deformation vibration range.

When $CH_2Cl_2$ is passed at different temperatures through the catalytic reactor over $\gamma$-$Al_2O_3$ as the catalyst, the conversion begins to be observed at 150°C and initial conversion of 100% is reached at 300°C (solid line in Fig. 1). However the catalyst undergoes deactivation so that at 300°C the initial 100% conversion drops to below 80% when the steady state is attained after about 20 min. Steady-state with 100% conversion is achieved only at 400°C (dotted line in Fig. 1). The products obtained in the steady-state

as a function of the reaction temperature are presented in Fig. 2. It may be seen that at low temperatures $CH_3Cl$ is formed as the intermediate product and desorbed:

$$CH_2Cl_2 \rightarrow CH_3Cl + HCl \, .$$

Hydrogen, required for this reaction to occur is initially supplied by surface OH groups. Selectivity to $CH_3Cl$ amounts to about 50%, the other half of the initial amount of $CH_2Cl_2$ introduced into the reactor being oxidized totally to $CO_2$ and HCl:

$$CH_2Cl_2 + O_2 \rightarrow CO_2 + HCl \, .$$
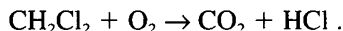
HCl is strongly held at the surface at lower temperature and begins to desorb only at 350°C. At temperatures higher than 450°C practically total conversion of $CH_2Cl_2$ to $CO_2$ and HCl takes place.

Let us discuss in more details the mechanism of the transformations of $CH_2Cl_2$ in the presence of oxygen. When $CH_2Cl_2$ is introduced on the catalyst at lower temperature (200°C), about 60% of it disappears, but no products except $CO_2$ are observed (Fig. 3). In the first minutes of the reaction the decrease of the conversion occurs and after 80 min the catalyst becomes totally deactivated. At 250°C, and even more at 300°C, $CH_3Cl$ begins to appear as a product after first few minutes of the reaction and its amount attains a certain constant level of the steady-state, corresponding to 20% or 80% conversion respectively.

The deactivation of the catalyst at low temperature is apparently due to the strong adsorption of both $CH_2Cl_2$ and HCl. Indeed, experiments, in which $CH_2Cl_2$ was adsorbed at 250°C in situ in the IR cell showed that it strongly interacts with the surface. Fig. 8 shows the IR spectra of $CH_2Cl_2$ in the gas phase and after adsorption on the surface of $Al_2O_3$. It may be seen that the frequencies of the rocking modes $r(CH_2)$ at about 1270 cm$^{-1}$ and of the bending modes $\delta(CH_2)$ at about 1465 cm$^{-1}$ [14] are shifted to considerably higher values. Simultaneously, in the range of stretching frequencies a new strong peak at 2940 cm$^{-1}$ appears. It may be suggested that adsorption of $CH_2Cl_2$ takes place as a two-sites process involving two adjacent exposed Al ions at the (111) plane of $Al_2O_3$. Two chlorine atoms of $CH_2Cl_2$ would occupy the oxygen vacancies above Al ions.
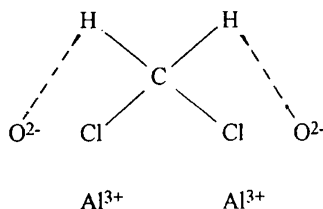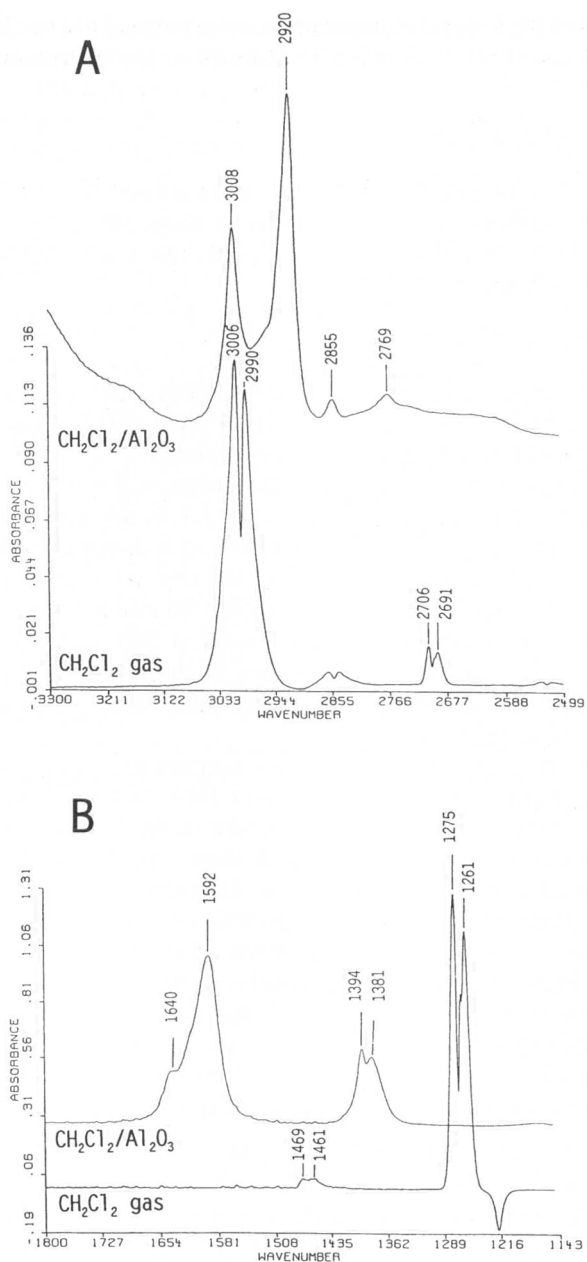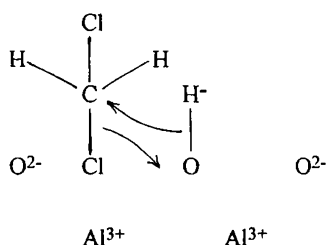


**Scheme 1.**

**Fig. 8.** The difference IR spectrum of $CH_2Cl_2$ after adsorption on alumina and outgassing at 250°C for 5 min (the spectrum of $Al_2O_3$ subtracted). The spectrum of pure $CH_2Cl_2$ is given for comparison. A) stretching vibration range, B) deformation vibration range.

This brings the two hydrogen atoms of the tetrahedron near neighbour oxide ions exposed above the surface and enables their strong interaction to form OH groups, which in turn will interact by hydrogen bonding with existing surface OH groups. Indeed, the difference spectra of $Al_2O_3$ after adsorption of $CH_2Cl_2$ presented in Fig. 9 show that all OH bands are involved in the interaction with the adsorbed $CH_2Cl_2$ and a huge band of hydrogen bonded OH groups appears.

If two-sites adsorption of $CH_2Cl_2$ is assumed at the surface of $Al_2O_3$, even at full coverage a certain number of isolated sites must be left unoccupied. In order to check this conclusion, the sample of $Al_2O_3$ after adsorption of $CH_2Cl_2$ was exposed to pyridine in situ in the IR cell and IR spectra were registered after outgassing at 150°C, 250°C, and 450°C (Fig. 9A and B). It may be seen that considerable amount of pyridine is adsorbed at the acid Lewis sites as indicated by the appearance of strong doublet at 1450 cm$^{-1}$/1455 cm$^{-1}$, and peaks at 1494 cm$^{-1}$ and 1625 cm$^{-1}$. It is evident that two types of Lewis sites of different acid strength exist at the surface. From those, which are responsible for the peak at 1450 cm$^{-1}$ pyridine is desorbed already at 250°C, whereas on those related to the peak at 1455 cm$^{-1}$, it is retained even after heating at 450°C when the adsorbed $CH_2Cl_2$ has already been removed from the surface as the result of its reaction to form $CO_2$ and HCl. It may be concluded that the isolated sites left unoccupied after adsorption of $CH_2Cl_2$ show strong Lewis acidity.

The unoccupied isolated Lewis acid sites at the surface may adsorb not only pyridine, but may also be involved in another possible type of adsorption of $CH_2Cl_2$, namely a single-site adsorption of this tetrahedral molecule through a chlorine apex:



**Scheme 2.**

If an OH group is present at the position next to the adsorbed molecule, rearrangement of the complex may take place, consisting in the splitting of the Cl−C bond and formation of a H−C bond, resulting in the desorption of $CH_3Cl$. This model finds its confirmation in the results of IR spectroscopic studies. Namely, it may be seen from Fig. 9A that after adsorption of $CH_2Cl_2$ on $Al_2O_3$ at 250°C four peaks appear in the stretching vibration range. Two strong ones at 3008 cm$^{-1}$ and 2920 cm$^{-1}$ are obviously due to the $\nu_{as}$ and $\nu_s$ vibrations in the $CH_2$ group of adsorbed $CH_2Cl_2$ [14]. Two
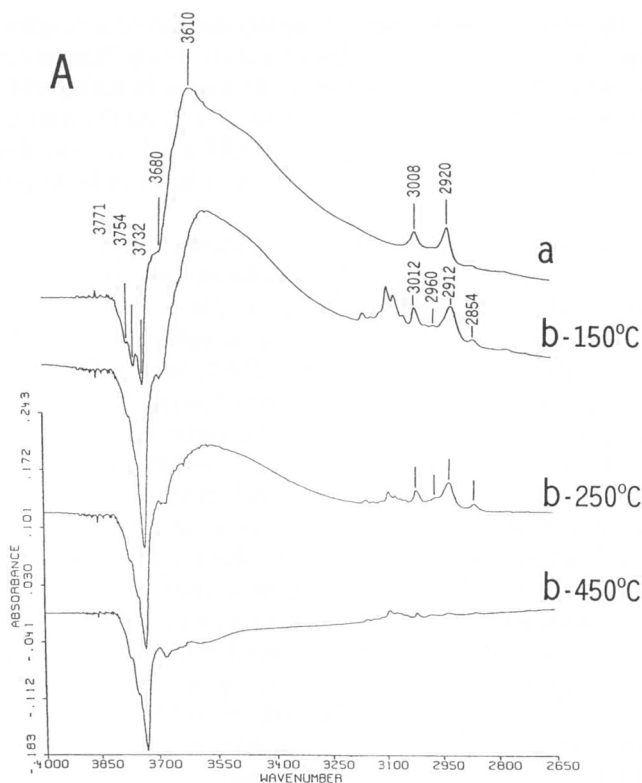
**Fig. 9.** The difference IR spectra of $CH_2Cl_2$ adsorbed on $Al_2O_3$ (a) and pyridine adsorbed on $Al_2O_3$ covered with $CH_2Cl_2$ and desorbed at different temperatures (b). The spectrum of $Al_2O_3$ registered before the experiment has been substracted. A) stretching vibration range, B) deformation vibration range.

other peaks at 2854 cm$^{-1}$ and 2960 cm$^{-1}$ may be assigned to the stretching vibration in the $CH_3$ group of $CH_3Cl$ formed at the surface as the result of the transformation represented by Scheme 2.

It is noteworthy that the intensity of these two peaks increases on raising the temperature to 250°C as could be expected because of the increasing rate of the attack of hydrogen on the adsorbed $CH_2Cl_2$ species.

After desorption of $CH_3Cl$ formed in the process shown by Scheme 2, the surface is left poisoned by chlorine atoms. Hydrogen from surface hydroxyl groups has been consumed in this process so that no more hydrogen is available to react with chlorine and desorb in form of HCl. The surface coverage with chlorine is determined by the ratio of the rates of reactions represented by Scheme 1 and 2. Indeed, Fig. 2 shows that HCl appears in
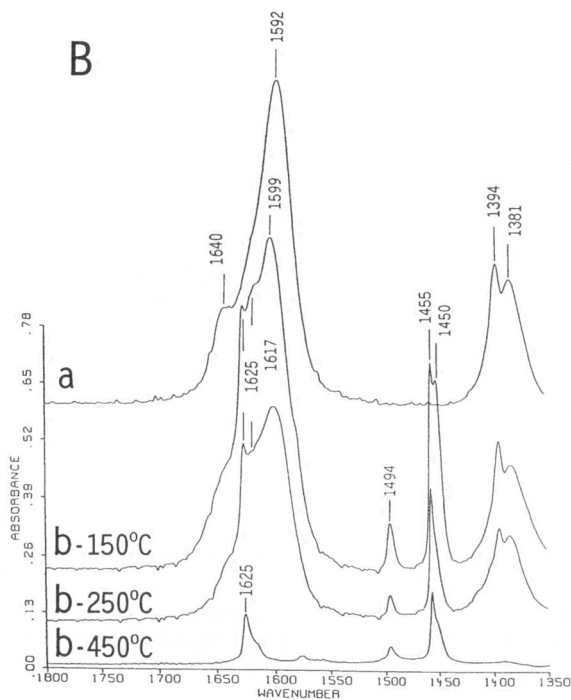
**Fig. 9B.**

the products in increasing amount only when the amount of $CH_3Cl$ decreases so that at 500°C practically the whole amount of chlorine introduced in the feed appears as HCl in the products.

The situation, represented in Fig. 3 changes dramatically when water vapour is added to the feed and an interesting phenomenon of oscillations of the conversion appears. This is shown in Fig. 4. The only chlorine-containing compounds found in the products formed in the course of this experiment are the initial reagent $CH_2Cl_2$ and $CH_3Cl$. The yield of the latter remains constant, whereas the amount of $CH_2Cl_2$ oscillates in a broad range indicating the oscillations of its consumption and hence the oscillations of the selectivity of $CH_3Cl$. It may be assumed that the reaction represented by Scheme 2:

$$CH_2Cl_2 + OH_s \rightarrow CH_3Cl + Cl_s + O_s$$
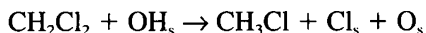
proceeds at a constant rate, its yield being constant, and that in the presence of water vapour some other process proceeds parallely consuming $CH_2Cl_2$ in an oscillatory way without producing HCl or $Cl_2$. The lack of HCl may be explained by assuming that hydroxylation of the surface by water pre-
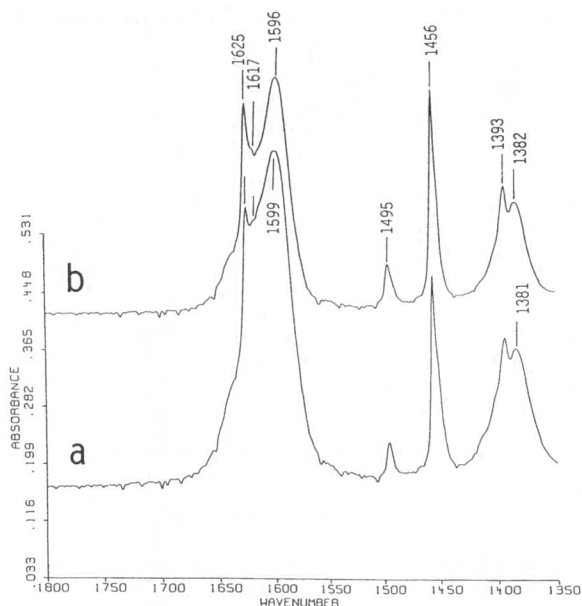
**Fig. 10.** The difference IR spectra of $Al_2O_3$ exposed to: a) the vapour of $CH_2Cl_2$, b) a mixture of $CH_2Cl_2$ and 24 Torr $H_2O$, both followed by exposure to pyridine and evacuation at 250°C. The spectrum of $Al_2O_3$ registered before the experiment has been substracted.

vents the Scheme 1 to operate because basic oxide ions become inaccessible for hydrogen from the $CH_2Cl_2$ due to blocking by hydrogen bonded water. In such circumstances the only possible further transformation is the extraction of Al ions from the lattice by desorption of alkyl aluminium chlorides, known to be stable volatile compounds [15]. Some confirmation of this hypothesis comes from the in situ IR measurements. Fig. 10 shows the IR spectra registered after exposing $Al_2O_3$ first to vapour of $CH_2Cl_2$, or the mixture of vapours of $CH_2Cl_2$ and 24 Torr of $H_2O$, in both cases followed by exposure to pyridine at room temperature and then evacuation at 250°C for 1 h. It may be seen that in the presence of water the peaks at 1382, 1393 and 1596 cm$^{-1}$ assigned to adsorbed $CH_2Cl_2$ are less intense. Two possibilities of further transformations may be envisaged. Either the surface layer composed of adsorbed $CH_2Cl_2$ and underlying $Al^{3+}$ ions must reconstruct before desorption of alkyl aluminium chloride can take place, or at 250°C the desorption removes the (111) facetting of (110) planes of the spinel lattice exposed and these planes must undergo reconstruction back to (111) facets before the adsorption of new molecules of $CH_2Cl_2$ can take
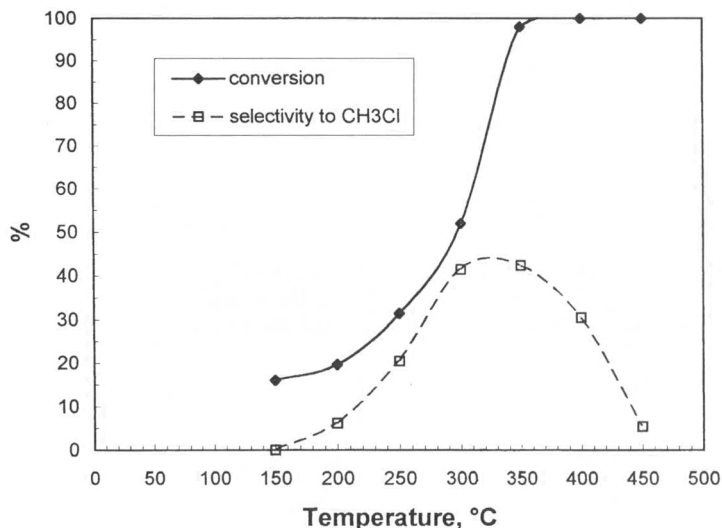
**Fig. 11.** CH₂Cl₂ conversion and selectivity to CH₃Cl in the steady state in the presence of water vapour in the feed as a function of temperature.

place. The necessity of such reconstruction in both alternatives may be the reason of the oscillatory behaviour of the system, as described for other systems [16].

At higher temperatures such reconstruction is rapid and the oscillator behaviour disappears. Instead, a steady state is established (Fig. 11) in which total conversion of CH₂Cl₂ is observed, whereas in the products only CH₃Cl is present and only at temperatures below 450°C. Simultaneously, the deposition of AlO OH was observed on the walls in the cool part of the reactor.

## Acknowledgement

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