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Catalytic Oxidation of Dichloromethane on γ-Al_2O_3: A Combined Flow and Infrared Spectroscopic Study

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When γ-Al_2O_3 is applied as a support for noble metals in the catalytic oxidation of dichloromethane, the reaction primarily takes place on the alumina. In our flow study, dichloromethane was completely converted at 600 K on γ-Al_2O_3, CO being a main product, especially at higher temperatures. Methyl chloride was observed in substantial amounts as an intermediate product. The formation of CH_3Cl, a reduction product formed under oxidative conditions, has been described before, but no satisfactory explanation has been given. To this end, reaction between alumina and CH_2Cl_2 has been studied by FTIR spectroscopy as well. The spectrum of the adsorbed species at 523 K was clearly different from that at 298 K. Apparently, dichloromethane reacted with surface hydroxyl groups, which disappeared. Experiments with CD_2Cl_2 enabled the identification of the surface species. The bands found could be attributed to surface methoxy groups and to adsorbed formate. With these species the products found in the flow experiments could be explained: the formates are converted into CO and the methoxy groups can react with HCl to form CH_3Cl.

The first step, reaction of the adsorbed dichloromethane with a surface hydroxyl group, yields a chloromethoxy species. This leads to a chemisorbed formaldehyde analogue, which appears to disproportionate due to some hydride shift, to form the observed methoxy and formate groups. The Cl from the CH_2Cl_2 is released as HCl and/or reacts with the alumina to form aluminum chlorides. The observed rate enhancing effect of added water in the gas stream can be explained by reaction with chlorinated alumina and restoration of surface hydroxyl groups, the active sites in the reaction with dichloromethane.

1. INTRODUCTION

Catalytic oxidation is one of the emerging technologies to reduce the release of chlorinated compounds into the environment (1–4). Catalysts for this process should be selective to HCl, carbon dioxide, and water, and resistant to chlorine. Both metal-oxide and noble metal-based catalysts are used for this process. Generally, chromium oxide is found to be the most active metal oxide for the catalytic combustion of chlorinated hydrocarbons (5, 6). However, it can form rather volatile and very toxic chromium oxychlorides, which eventually leads to deactivation (7).

Noble metals are active catalysts in chlorinated hydrocarbon combustion (8–11). Formation of noble metal (oxy)chlorides is observed (12), but these are less susceptible to volatilization. Interaction of Pt and Pd with chlorine is observed to promote the formation of highly chlorinated by-products, e.g., polychlorinated benzenes from chlorobenzene (13, 14). The support material plays an important role in the destruction mechanism. Noble metal catalysts for catalytic oxidation of chlorinated compounds are supported on various materials, e.g., zeolites (13) and TiO_2 (15), but most frequently γ-Al_2O_3 is used. Whindawi and Zhang observed a completely different reactivity toward chlorinated methanes for Pt supported on TiO_2 and Al_2O_3, respectively (15). The reaction of dichloromethane (CH_2Cl_2) is particularly interesting in this light. The rate of CH_2Cl_2 conversion for Pt on γ-Al_2O_3 and plain γ-Al_2O_3 is exactly the same (16). The only difference is the product distribution. With a Pt containing catalyst at 723 K CH_2Cl_2 is converted into CO_2, while on alumina alone CO is the major carbon containing product. In both cases, methyl chloride (CH_3Cl) is observed as a by-product (15, 17). Formation of CH_3Cl, formally a reduction product, is rather unexpected in an oxidative environment. The decomposition of CH_2Cl_2 on γ-Al_2O_3 has been studied by Haber *et al.*, using IR spectroscopy (17). They suggest a mechanism for methyl chloride formation in which a hydride (H^-) from the surface reacts with an adsorbed dichloromethane molecule. However, conceptually a hydride shift from an hydroxyl group seems highly unlikely.

Therefore, we have studied the surface reaction of CH_2Cl_2 on γ-Al_2O_3 by means of flow techniques and FTIR spectroscopy to elucidate the ruling mechanism(s).

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2. METHODS

2.1. *Catalyst*

The surface area of the γ-Al_2O_3 (Rhône Poulenc, Crystal structure confirmed by X-ray diffraction) is 206 m^2/g, as measured by liquid nitrogen adsorption. Particle size distribution in the flow experiments was between 125 and 250 μm.

2.2. *Flow Experiments*

Gases were introduced by electronic mass flow controllers (Brooks 5850 E). Teflon tubing was used to prevent metal wall mediated reactions. All tubes and the injection valves of the GC were heated to prevent condensation of products.

For each experiment 0.30 g (~0.6 ml) of the catalyst was placed in a Pyrex microreactor (internal diameter = 5 mm, bed height about 30 mm). The total gas flow was 50 ml/min: 1000 ppm CH_2Cl_2, 89% Helium, 10% oxygen (Air Liquide, 99.9%), and 1% water. A stream of 1000 ppm dichloromethane (Carlo Erba, >99%) was obtained by addition of a known amount of CH_2Cl_2 to a gas bottle, which was pressurized with helium (Air Liquide). Water was added to the gas stream by bubbling He through an impinger.

The effluent gases were analyzed by two on-line GCs (Varian Star 3400CX) provided with a FID detector. The first GC was equipped with a packed column (Hayesep D) and a methanizer to analyze CO and CO_2. The analysis was calibrated by injecting a known amount of CO_2. The second GC-FID was equipped with a capillary column (Restek RTX) and used for analysis of organic compounds. Conversion was calculated using the surface area of the CH_2Cl_2 peak, relative to the one obtained by bypassing the reactor to provide a blank value. The amount of CH_3Cl was calculated from the CH_2Cl_2 peak, using a relative response factor of 0.9. A Fisons QTMD mass spectrometer operating at 70 eV was also connected to the setup, to allow on-line real-time-resolved measurements.

A typical experiment started by heating the catalyst under a He/O_2 flow to 623 K. After 1 h to allow the flow to stabilize, CH_2Cl_2 was added and the effluent of the reactor was monitored by the mass spectrometer. About 3 h is necessary to reach a stationary state. These conditions were maintained overnight, whereafter the catalyst was cooled to 423 K, and conversion and products were analyzed by GC. Subsequently the temperature was raised (5 K/min, in steps of 25 K), and after a stabilization time of about 20 min, effluent gases were analyzed.

2.3. *FTIR Measurements*

About 10 mg of the catalyst was pelleted as a disc 12 mm in diameter. The spectra were taken in a vacuum device, which consisted of a cell with KBr windows. The disc was mounted into the cell and then was lifted into an oven. Subsequently, the system was evacuated at ambient temperature ($p = 10^{-5}$ mbar), and the alumina was heated slowly (5 K/min) to 623 K and left at this temperature for 1 h, to eliminate adsorbed water and part of the OH groups. According to Knözinger and Ratnasamy (18), this treatment leaves about 6×10^{14} OH-groups cm^{-2} on the alumina surface.

All spectra were recorded at room temperature on a Nicolet 5DXC FTIR spectrometer averaging 32 scans with a 2 cm^{-1} resolution and analyzed using OMNIC software. A 13-point smoothing was performed. The spectrum recorded after the thermal treatment (Fig. 3a) was used for subtraction as a blank (subtraction factor = 1). Next, 2.4 mbar of dichloromethane or dichloromethane-d_2 (CD_2Cl_2, Aldrich) was introduced into the cell at 298 K, and after 10 min spectra were recorded of both the gas phase and the disc. Subsequently, the disc was lifted from the IR beam and a spectrum of the gas phase in the cell was taken. The spectra shown for the adsorbed dichloromethane at 298 K were obtained by subtracting the spectrum of the blank catalyst and of the gas phase (subtraction factor = 1). Next, the disc was lifted into the oven and maintained at 523 K for 30 min; this period was sufficient to arrive at stationary state. After evacuation the pellet was reintroduced into the beam and after cooling a spectrum was recorded, showing the peaks of the adsorbed species on the catalyst.

3. RESULTS

3.1. *Flow Experiments*

First, the γ-Al_2O_3 was heated in He/O_2 to 573 K, then the reactor was bypassed and the flows of CH_2Cl_2, He, O_2, and water were adjusted. The flow was allowed to stabilize, until the MS signal of CH_2Cl_2 (mass 49, which gives a higher signal than the molecular ion 84) was constant. Then the flow was switched over the reactor again (time = 0 min) and the MS signals are followed as shown in Fig. 1.

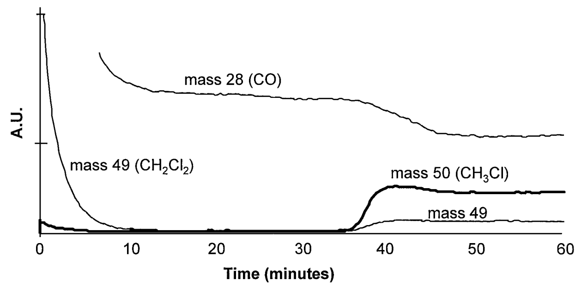


FIG. 1. Initial behavior of dichloromethane on γ-Al_2O_3 at $T = 573$ K. Conditions: 0.30 g γ-Al_2O_3, flow = 50 ml/min, 1000 ppm dichloromethane, 10% O_2, 1% H_2O, and 89% He. At time = 0 min, the catalyst was exposed to the reaction mixture.

When the catalyst is exposed to dichloromethane at 573 K, the mass 49 signal decreases rapidly to zero. Just after the CH_2Cl_2 containing flow is switched from the bypass to the reactor a high-intensity mass 28 is observed. This is probably due to the N_2 signal of air which enters the MS during switching the bypass valve. After about 10 min the mass 28 signal becomes stable, and we assume that this corresponds to CO. During a period of about 25 min, CO is the only compound leaving the reactor. Then the CO signal decreases, mass 50 (CH_3Cl) appears, and mass 49 reappears. After 10 min the signal intensities become stable. At this level about one-third of the mass 49 (CH_2Cl^+) signal is due to fragmentation of CH_3Cl; the rest of the signal comes from CH_2Cl_2 and corresponds to a conversion of 92%. Hydrochloric acid (mass 36, not shown in the graph) appears only after several hours, probably after the γ-Al_2O_3 surface is saturated. This product mixture remains stable overnight. In similar experiments, Haber *et al.* (17) observed oscillations in the conversion of dichloromethane, while CH_3Cl production remained constant. We could not reproduce these results, but conditions were not exactly the same and Haber *et al.* used a different brand of γ-Al_2O_3.

Figure 2 shows the conversion curve of dichloromethane and intermediate products formed over γ-Al_2O_3. At higher temperatures CO is the major product and small amounts of CO_2 are observed. During the course of the experiment (which lasts about 30 h) the carbon balance decreases from 95% at 598 K to 60% at 773 K. Furthermore, the catalyst becomes darker, which indicates deposition of carbonaceous material. This may entail deactivation of the alumina. Between 473 and 773 K, CH_3Cl is observed, reaching its maximum production at around 600 K (40% based on dichloromethane input, which then is completely converted). Compared to MS analysis, conversion at 573 K is slightly lower: 88%.

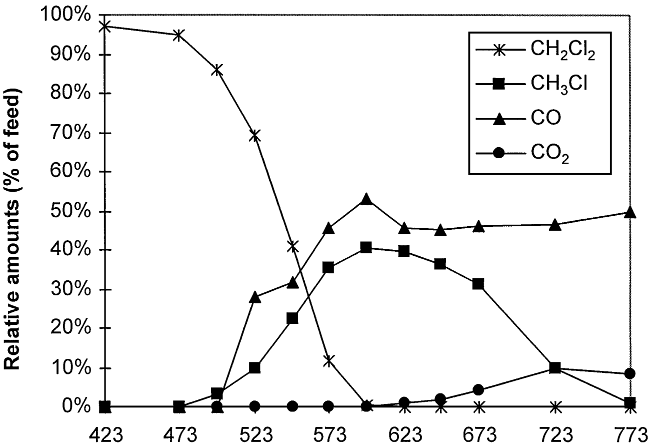


FIG. 2. Flow results: relative amounts of dichloromethane and products against temperature. Conditions: 0.30 g γ-Al_2O_3, flow = 50 ml/min, 1000 ppm dichloromethane, 10% O_2, 1% H_2O, and 89% He.

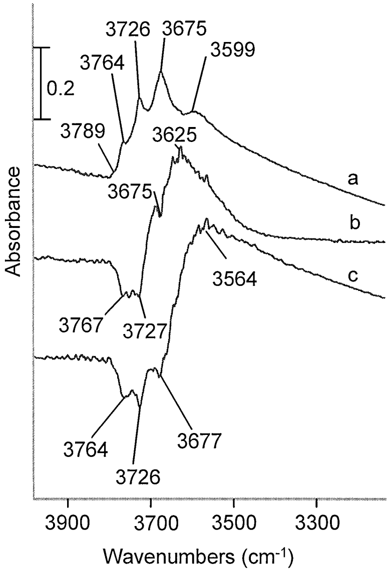


FIG. 3. FTIR spectra of the O–H stretching frequency range showing the consumption of surface hydroxyl groups. (a) Alumina heated at 623 K. (b) After addition of 2.4 mbar of CH_2Cl_2 at 298 K for 10 min, and after subtraction of the gas phase and of the blank spectrum (spectrum a) (this applies also to the b spectra in the other figures). (c) Upon reaction of CH_2Cl_2 at 523 K for 30 min, after evacuation of the gas phase and after subtraction of the blank spectrum (this applies also to the c spectra in the other figures).

In these experiments 1% of steam was present in the feed. In the catalytic combustion of chlorinated hydrocarbons water may promote formation of HCl rather than Cl_2 (10). Furthermore, addition of steam improves conversion: the temperature of 50% conversion is 543 K in the presence of water, but increases to 593 K in the absence of water. Product composition was comparable: methyl chloride is also formed as an intermediate, albeit in a slightly reduced amount (31% at 600 K).

3.2. *FTIR Spectroscopic Results*

Figure 3 shows the O–H stretching frequency range of the γ-Al_2O_3 disc pretreated at 623 K before reaction with CH_2Cl_2 (spectrum 3a). Distinct types of surface hydroxyl are observed, which can be ascribed, following Knözinger and Ratnasamy (18), to OH groups attached to one or more Al ions. The large tail below 3600 cm^{-1} indicates that some hydrogen-bonded OH groups and strongly adsorbed water are still present on the surface. When CH_2Cl_2 is introduced at 298 K, and spectrum 3a is subtracted, negative features at 3767, 3727, and 3675 cm^{-1} are observed (spectrum 3b). This indicates interaction of the adsorbed dichloromethane with surface OH groups. The broad peak at lower wavenumbers becomes larger, so probably dichloromethane forms hydrogen bonds with the surface hydroxyl groups.

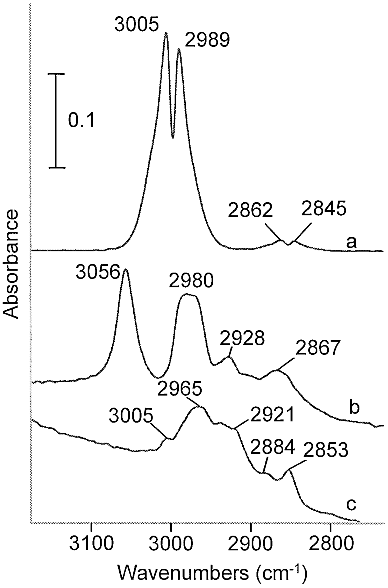


FIG. 4. FTIR spectra showing the C–H stretching vibration range. (a) Gas phase spectrum of dichloromethane. (b) Adsorption of CH_2Cl_2 at 298 K. (c) Reaction of CH_2Cl_2 at 523 K.

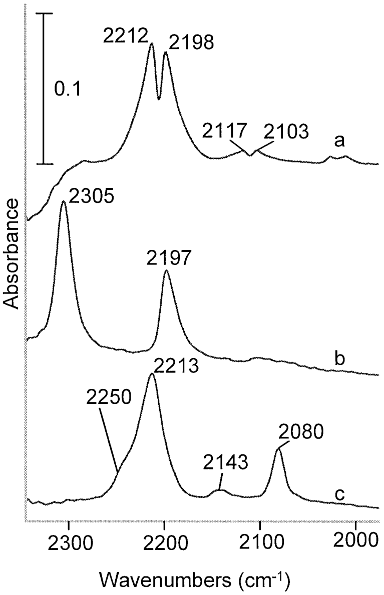


FIG. 5. C–D stretching vibration range. (a) Gas phase spectrum of dichloromethane-d_2. (b) Adsorption of CD_2Cl_2 at 298 K. (c) Reaction of CD_2Cl_2 at 523 K.

Spectrum 3c shows the ν(O–H) region after reaction of CH_2Cl_2 at 523 K and after removal of the gas phase. The negative peaks are more prominent than in the spectrum at 298 K. The large band of hydrogen bonded hydroxyl groups is shifted to lower frequency, indicating that a different type of hydrogen bonding is present at 523 K than at 298 K.

In Fig. 4 the C–H stretching region is shown. The spectrum of gas phase CH_2Cl_2 (spectrum 4a) shows a strong doublet at 3005/2989 cm^{-1}. Adsorption of dichloromethane at 298 K (spectrum 4b) yields two major bands at 3056 and 2980 cm^{-1}. After reaction of dichloromethane at 523 K the adsorption at 3056 cm^{-1} has entirely disappeared, indicating that at 523 K different species are present on the surface than at 298 K. Major peaks are located at ~2965, 2921, and 2853 cm^{-1}.

To facilitate attribution of the peaks, the reaction of CD_2Cl_2 was also studied. In Fig. 5 the C–D stretching region is shown. Compared to CH_2Cl_2, the doublet in the gas phase spectrum (5a) is shifted to 2212/2198 cm^{-1}. In spectrum 5b of the CD_2Cl_2 adsorbed at 298 K, two peaks are observed at 2305 and 2197 cm^{-1}. Again, the picture after reaction at 523 K is more complex. Important features are seen at 2213 and 2080 cm^{-1}.

At lower frequencies, the gas phase spectrum of dichloromethane (Fig. 6a) shows peaks at 1276/1260 cm^{-1}. In spectra of adsorbed species on Al_2O_3, it is not possible to identify peaks below ~1000 cm^{-1} due to the strong Al–O signals, so C–Cl vibrations cannot be seen. In spectrum 6b of CH_2Cl_2 adsorbed at 298 K, the peaks around 1270 cm^{-1} remain, although the intensities change. After dichloromethane had reacted at 523 K (6c), a completely different spectrum is obtained, with peaks at 1591, 1468, 1393, 1380, and 1091 cm^{-1}.

In Fig. 7 the spectra of gas phase CD_2Cl_2 (7a) and CD_2Cl_2 adsorbed at 298 K in the C–D deformation and C–O stretching frequency range are shown. Spectrum 7c refers to this region after reaction of dichloromethane-d_2 at 523 K. Some peaks show only a small shift compared to spectrum 6c, while other peaks are shifted to a larger extent.

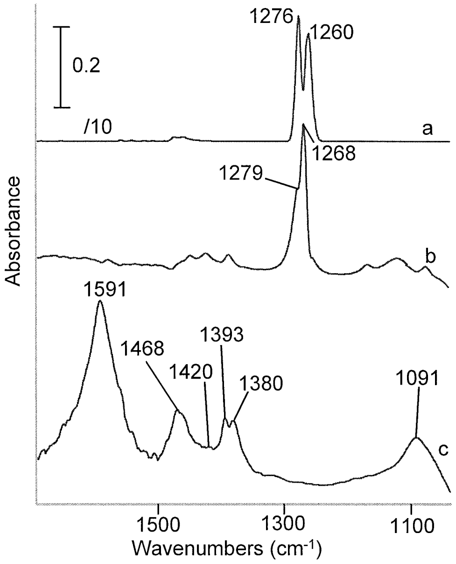


FIG. 6. C–O stretching and C–H bending vibration ranges. (a) Gas phase spectrum of dichloromethane. (b) Adsorption of CH_2Cl_2 at 298 K. (c) Reaction of CH_2Cl_2 at 523 K.

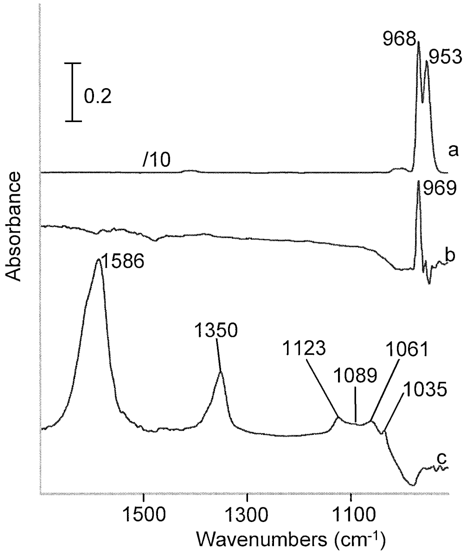


FIG. 7. C–O stretching and C–D bending vibration ranges. (a) Gas phase spectrum of dichloromethane-d_2. (b) Adsorption of CD_2Cl_2 at 298 K. (c) Reaction of CD_2Cl_2 at 523 K.

4. DISCUSSION

4.1. Assignment of Peaks and Comparison to Literature

The peaks in the spectrum of the OH groups (Fig. 3a) can be ascribed in accordance with Knözinger and Ratnasamy (18): the small feature at 3789 cm^{-1} stems from the Ib-type OH group. The signal at 3764 cm^{-1} is due to the Ia species, attached to a tetrahedral coordinated Al^{3+} ion. This group shows the largest interaction with CH_2Cl_2 adsorbed at 298 K (spectrum 3b). The bands at 3726 and 3675 cm^{-1} can be assigned to the type IIa and III OH groups, respectively. These latter two OH groups show only little interaction with dichloromethane adsorbed at 298 K. At 523 K all OH groups react with CH_2Cl_2.

The spectrum after dichloromethane adsorption at 298 K shows some differences compared to the gas phase spectrum. The asymmetric C–H stretch (Fig. 4) is affected more than the symmetric one (the former shift from 3005 to 3056 cm^{-1}, while the latter shift from 2989 to 2980 cm^{-1}). Likewise, in the spectrum of deuterated dichloromethane (Fig. 5), $\nu_{as}(CD_2)$ is shifted from 2212 to 2305 cm^{-1}, while $\nu_s(CD_2)$ remains the same. The shift in the asymmetric stretch vibration is larger in the case of the deuterated dichloromethane. This can be understood when taking into account that at 298 K hydroxyl groups are involved in hydrogen bonding (spectrum 3b). If a hydrogen from CH_2Cl_2 interacts with an OH group, the shift in the stretch vibration is different from when a deuterium from CD_2Cl_2 interacts with an OH group.

Comparison of the spectra after reaction of CH_2Cl_2 with γ-Al_2O_3 at 523 K (Figs. 4c and 6c) and CD_2Cl_2 (Figs. 5c and 7c) permits the attribution of the bands to adsorbed bidentate formates and monodentate and bidentate methoxy species (see Table 1). In Figs. 6 and 7, bands at 1591 (1586 for CD_2Cl_2), 1380 (1350), and 1091 (1061) cm^{-1} are shifted only slightly for the hydrogenated and deuterated molecules. Bands at 1592 and 1380 cm^{-1} have also been observed by Haber *et al.* (17), who attributed these to deformation vibrations of CH_2 of dichloromethane adsorbed on Al_2O_3. However, our results with deuterated dichloromethane show that this assignment is not correct, since the bands should be shifted to lower frequencies.

Peaks which are not shifted much likely arise from C–O stretch vibrations. The bands at 1591 and 1380 cm^{-1} are near those observed for the asymmetric and symmetric stretch vibrations of COO of bidentate formates (19–21). These bands were also observed by Greenler in his study of methanol adsorption on alumina (22). The shift of the $\nu_s(COO)$ peak (30 cm^{-1}) is larger than that of $\nu_{as}(COO)$ (5 cm^{-1}), because for the asymmetric stretch the hydrogen (or deuterium) atom moves in phase with the carbon atom (22). The band at 1091 (1061) cm^{-1} can be due to the ν(C–O) vibration of a mono- or bidentate methoxy species, although Beebe *et al.* (23) found the peak at higher frequency (1055 cm^{-1}). The shift upon deuteration with 30 cm^{-1} to lower frequency is in accordance with the shift of this band on some other catalysts (24, 25).

The band at 1468 and the very small feature at 1420 cm^{-1} (Fig. 4c), situated in the frequency area of carbonates, cannot be ascribed to oxygenated species since they are shifted

TABLE 1

Assignments of Vibrational Modes for Methoxy and Formate Species and Comparison to Literature

Mode	This study [a,b] adsorbed 523 K	Comparison to literature [a,b]		
		CH_3O-monodentate [c]	CH_3O-bidentate [d]	Formate bidentate [e]
$\nu_{as}(CH_3)$	2963 (2213)	2960 (2255)		
$\nu(CH_3)$	2921 (2143)		2921 (2152)	
ν(H–C)	2884 (n.o.)			2870
$\nu_s(CH_3)$	2853 (2080)	2850 (2089)		
$\nu_{as}(COO)$	1591 (1586)			1597 (1587)
$\delta_s(CH_3)$	1468 (1123)	1475 (1119)		
$\delta_{as}(CH_3)$	1420 (1089)	1420 (1086)		
δ(H-C)	1393 (1035)			1394 (1034)
$\nu_s(COO)$	1380 (1350)			
νCO	1091 (1061)	1055 (1067)		

Note. n.o., not observed.

[a] Frequencies in cm^{-1}.

[b] For CH_2Cl_2, in parentheses for CD_2Cl_2.

[c] From adsorption of CH_3Cl on alumina (23).

[d] From methoxy species on CeO_2 (41).

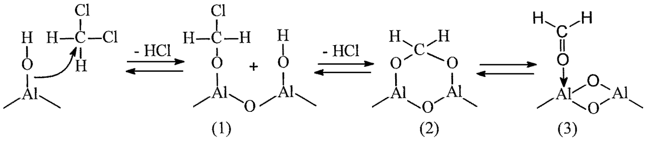
[e] From reactions of methanol on alumina (22) and studies on sodium formate (19).

in the experiment with CD_2Cl_2 (Fig. 5c). They must therefore arise from species containing hydrogen or deuterium. Both peaks are also found by Beebe *et al.* upon reaction of methyl chloride with alumina (23). We assign the peaks at 1468 (1123) and 1420 (1089) cm^{-1} to the asymmetric and symmetric bending modes of surface methoxy groups, respectively. As well as some other bands in the ν(C-H) region, these bands were not observed by Haber *et al.* (17). This could be due to our higher CH_2Cl_2 concentration, which yielded a higher surface coverage, which promotes the formation of monodentate methoxy species (*vide infra*). The band at 1393 cm^{-1} can be attributed to the deformation of the C–H of the formate species. The shift of this band to 1035 cm^{-1} in the experiment with deuterated dichloromethane is in accordance with Greenler's results (22). The C–H stretch of the formate has been observed as a very small band at 2884 cm^{-1}.

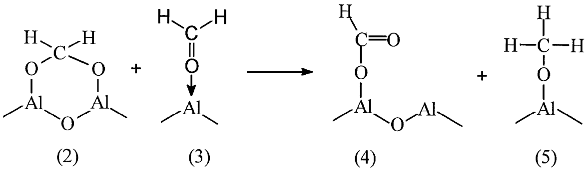
Ramanchandran *et al.* (26) observed an additional band at 1790 cm^{-1} after adsorption of CH_2Cl_2 on a cobalt-exchanged Y zeolite. They attributed this band to a CHOCl surface species, referring to a publication by Fevrier *et al.* (27) in which this species is only a speculation. This peak is indeed in the area of ν(C=O) of acyl chlorides (28). However, they also observe bands at 2976 and 2850 cm^{-1}, which they ascribe to the ν_{as} and ν_s vibrations of the CH_2 in dichloromethane. This is at variance with our gas phase spectra. Possibly, Ramanchandran *et al.* (26) had obtained some gas phase methyl formate ($\nu(C{=}O) = 1768\ cm^{-1}$ (29)). However, this hypothesis should be confirmed by tests with CD_2Cl_2. This band has not been observed in our study of adsorption on alumina, but this could be due to the difference in catalyst and operating conditions.

4.2. Mechanism

In the previous section was shown that two kinds of species originate from reaction of dichloromethane with γ-alumina at 523 K: surface methoxy groups and adsorbed formate. A first step in the mechanism leading to these species could be the displacement of a chlorine of dichloromethane on the alumina surface. Krawietz *et al.* (30) observed in solid state ^{13}C-NMR on a Zn-Y zeolite that ^{13}C-labeled dichloromethane can interact with a surface OH group to form a chloromethoxy species (species (1) in Scheme 1). This species is stable at 298 K, but decomposes with dealumination of the zeolite at 423 K as observed by ^{27}Al-NMR. The main product of decomposition of CH_2Cl_2 on this zeolite is CO, as in our experiments. Analogously, it is documented that in the aqueous phase dichloromethane reacts with water by a S_N2 substitution reaction to produce HCl and chloromethanol (CH_2ClOH) (31), which is equivalent to the species observed by Krawietz (30). The latter product decomposes to HCl and formaldehyde. Under our conditions surface OH groups can play the role of water. Indeed, hydroxyl groups are consumed in the reaction (Fig. 3). Free formaldehyde is not observed in either flow or FTIR experiments. Probably no free formaldehyde is formed, meaning that species (1) is converted into some chemisorbed formaldehyde analogue, for example, (2) and/or (3), the latter involving formaldehyde sorbed at an alumina Lewis acid site.



SCHEME 1



SCHEME 2

The chloride displaced in the first and second stages of Scheme 1 can react with surface Al^{3+}, giving an aluminum chloride species, or pick up a proton to form HCl. HCl is known to react with alumina under our conditions (32), so probably the surface of γ-Al_2O_3 becomes partly chlorinated in the process.

It is clear that a disproportionation—involving some hydride shift—is required to arrive from species like (2) and (3), at the observed formate (4), and methoxy groups (5). This type of conversion is known as the Cannizzaro reaction. It is usually described as taking place in solution under strongly alkaline conditions (33), but is also known to proceed with acid catalysis (34). Alumina is a more acidic than a basic catalyst (35), so an acid-type Cannizzaro reaction is more likely. In (sulfuric acid) solution, formaldehyde can be converted into the hydroxycarbenium ion, HO–CH_2^+, which is stated to accept a hydride from hydrated formaldehyde, HO–CH_2–OH (34). In our case species (3) and (2), respectively, can react likewise, as illustrated in Scheme 2.

Closely related to the Cannizzaro reactions is the acid-catalyzed Tishchenko reaction: two formaldehyde entities give a methyl formate molecule. The latter product was not seen in our IR study or our flow experiments, so we tend to rule out this pathway.

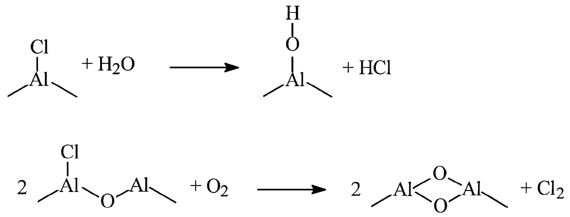
Haber *et al.* (17) have proposed that the formation of CH_3Cl occurs by a hydride transfer from the surface to an adsorbed dichloromethane molecule. From their IR spectra they concluded that at 523 K CH_2Cl_2 is coordinated with the chlorine atoms to O^{2-} ions on the alumina. Our experiments with deuterated dichloromethane show that this proposal is not correct. Furthermore, according to the authors hydrogen would be provided as a hydride by the surface hydroxyl groups. This is against the known relative electronegativity of oxygen and hydrogen, and therefore must be discarded. Moreover, in the case of deuterated dichloromethane, if hydrogen originates from the surface, the formed methyl chloride should be CD_2HCl. However, the surface methoxy species we observed were CD_3O species, and not CD_2HO species. Characteristic adsorption bands of the latter species at 2177 and 2131 cm^{-1} (36) were not found. Therefore, hydride transfer from the surface OH groups does not occur. Direct hydride transfer to adsorbed CH_2Cl_2 might be possible, when a species like (2) is considered as the hydride donor. This would yield surface formate and gas phase methyl chloride. Reaction of gas phase methyl chloride with alumina would yield methoxy groups (23). But the characteristic vibrations of CH_3Cl (2968 and 1355 cm^{-1} (37)) were not observed in the gas phase after reaction of CH_2Cl_2 at 523 K. And even if it were present in very small amounts, the large excess of CH_2Cl_2 present in the gas phase makes CH_3Cl as an important source for surface methoxy groups very unlikely.

It is of interest to compare the behavior of CH_2Cl_2 with that of CCl_4, as studied by Clet *et al.* (32). On hydroxylated alumina it first reacts with a surface hydroxyl group, forming a trichloromethoxygroup and HCl, which then reacts with a second surface hydroxyl group to form phosgene ($COCl_2$) and HCl. This compound is more stable than formaldehyde and is indeed observed by Clet. They also studied dehydroxylated alumina; phosgene is formed as well, but aluminum chlorides are formed instead of HCl.

Dai *et al.* (38) studied the decomposition CF_2Cl_2 on alumina dehydroxylated at 1000 K, which leaves only few OH groups. This dehydroxylated alumina has very active coordinatively unsaturated Al^{3+} sites, which are able to dissociate CF_2Cl_2 to form carbonates already at temperatures even below 300 K. When the alumina was pretreated at only 623 K (which is the dehydroxylation temperature we use), no reactivity was found toward CF_2Cl_2 at these low reaction temperatures. So in our case, in the presence of surface hydroxyl groups, the very active Al^{3+} sites are not accessible.

With the observed surface species, the products found in the flow experiments, CO and CH_3Cl, can be explained. The adsorbed formate species decomposes to form CO or, to a lesser extent, is oxidized to CO_2. The reaction of the surface methoxy species with formed hydrochloric acid would provide the methyl chloride observed.

The formation of the methoxy species requires a certain surface concentration of the chemisorbed formaldehyde, species (2) and (3). This could explain the observation that in Fig. 1 methyl chloride is formed only after a certain induction period. In the beginning the surface concentration of species (2) and (3) is too low for disproportionation (Scheme 2). After a certain time the surface concentration is high enough to allow formation of methoxy groups and subsequent CH_3Cl formation. Analogously, due to the high surface coverage, not all dichloromethane can react and CH_2Cl_2 reappears in the MS spectrum. The initial selectivity to CO can be explained by thermal decomposition of isolated chemisorbed formaldehyde.



SCHEME 3

At higher temperatures species (2) and/or (3) could be decomposed rapidly and desorb more easily, making disproportionation less likely. At these temperatures methyl chloride, if still intermediately formed, may also be decomposed on γ-Al_2O_3 (23). This is in agreement with the flow experiments, where CH_3Cl is not observed as a product at higher temperatures. Interestingly, following this scheme, oxygen is not necessary for the production of both major products, CO and CH_3Cl. Indeed, Bond and Rosa (39) found that conversion of CH_2Cl_2 also takes place around 700 K in an atmosphere of only N_2 and water.

As stated above, alumina will be chlorinated during the course of the reaction. Reaction with water can regenerate surface hydroxyl groups, as depicted in Scheme 3. According to Clet *et al.* (32), in the absence of water, chlorinated alumina might react with O_2, forming aluminum-oxide bonds and Cl_2. But this is not probable under our conditions, as alumina is a very poor “Deacon” catalyst, releasing Cl_2 only above 1000 K (40).

From our flow studies water is known to improve the rate of conversion of dichloromethane. The fact that the product distribution is the same in the presence and absence of water indicates that an identical mechanism is operative. The role of water is primarily to increase the concentration of surface hydroxyl groups and to regenerate these from Al–Cl entities (39). When the catalyst was first exposed to the reaction mixture at 573 K, HCl was only observed after several hours, indicating that the regeneration of the chlorinated alumina surface is not easy.

5. CONCLUSIONS

Dichloromethane reacts with γ-Al_2O_3 at moderate temperatures, to form CO and CO_2 as end products. Methyl chloride, a reduction product, is also formed; up to 40% of CH_2Cl_2 is converted into CH_3Cl at around 600 K. The presence of mono- and bidentate methoxy groups and bidentate formates on the γ-Al_2O_3 surface has been confirmed by using deuterated dichloromethane in FTIR experiments.

These groups are all fully deuterated, proving that hydrogen on the surface (from the hydroxyl groups) is not involved in the mechanism. The proposed first step is reaction with a surface hydroxyl group, consonant with the observation that the IR bands of the surface OH groups disappear upon reaction with CH_2Cl_2. This results in a chloromethoxyl species which gives chemisorbed formaldehyde (species (2) and (3) in Scheme 1). Analagous to the acid-catalyzed Cannizzaro reaction, species (2) and (3) could disproportionate on the surface, yielding surface methoxy groups (4) and adsorbed formate species (5).

The surface formates can react further to CO or CO_2. The methoxy species can react with HCl to form methylchloride. A striking aspect of the proposed mechanism is that first both chlorines of CH_2Cl_2 are removed and then Cl re-enters by nucleophilic displacement on a surface methoxy species. The mechanism explains both product formation in the flow experiments and the observations after first exposure of alumina to CH_2Cl_2 (Fig. 1). After an induction period, in which a surface concentration sufficient for the reaction of adsorbed species is built up, CH_3Cl starts to appear.

The addition of water to the feed was found to increase the rate, by increasing the number of active sites (i.e., hydroxyl groups) on the surface. Water also regenerates the Al–Cl entities, formed either directly by reaction of dichloromethane or by reaction of HCl.

A disadvantage of alumina as a catalyst for the oxidation of dichloromethane is that CO is formed, while CO_2 is preferred, and that it will lose its activity by deposition of carbonaceous material. The catalyst can be much improved by the addition of a small amount of Pt (or presumably any other metal active in CO oxidation). It has been shown that Pt/Al_2O_3 can convert dichloromethane with 100% selectivity to CO_2, although the rate of conversion of CH_2Cl_2 does not increase (16).

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