ELSEVIER

Catalysis Today 54 (1999) 65–79

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Mechanism of catalytic destruction of 1,2-dichloroethane and trichloroethylene over γ-Al_2O_3 and γ-Al_2O_3 supported chromium and palladium catalysts

Manon M.R. Feijen-Jeurissen [a,*], Jelle J. Jorna [a], Bernard E. Nieuwenhuys [a], Gilles Sinquin [b], Corinne Petit [b], Jean-Paul Hindermann [b,1]

[a] *Department of Heterogeneous Catalysis and Surface Chemistry, Leiden Institute of Chemistry, Leiden University, P.O. box 9502, 2300 RA Leiden, The Netherlands*

[b] *Laboratoire d'Etude de la Réactivité Catalytique, des Surfaces et Interfaces, ECPM – UMR CNRS-ULP 7515, 25, rue Becquerel, 67087 Strasbourg Cedex 2, France*

Abstract

The destruction mechanisms of C_2-chlorinated hydrocarbons have been investigated. The adsorption of 1,2-dichloroethane (DCE) and trichloroethylene (TCE) on alumina and alumina supported catalysts was studied by FTIR-spectroscopy. Interpretation of the spectra suggests that the destruction of DCE occurs via HCl elimination to vinyl chloride, followed by an attack of a hydrogen and a surface oxygen on the double bond resulting in acetyl chloride. Subsequent elimination of a chloride ion gives acetaldehyde that can be further oxidized into acetate. With regard to the destruction of TCE, the spectra indicate that TCE is attacked by a basic oxygen and a hydrogen according to Markovnikov's rule. This results in the formation of acyl chloride, which is further converted into acetate like species. In addition, the oxidation of TCE was examined over alumina supported catalysts. While alumina itself is not very active, palladium and chromium containing catalysts are. In the absence of water, the formation of tetrachloroethylene (PCE) was observed. Addition of water to the feed resulted in a decrease in the amount of PCE produced. Although water did not affect the TCE conversion over palladium it inhibited the oxidation reaction over chromium oxide. The activity of the chromia catalyst compared to alumina might be due to the supply of basic oxygen which can attack the double bond. The inhibitive effect of water on the conversion of TCE is probably due to blocking of active oxygen sites. ©1999 Elsevier Science B.V. All rights reserved.

Keywords: 1,2-dichloroethane; Trichloroethylene; Palladium catalysts; Chromia catalyst; Alumina; IR-spectroscopy

1. Introduction

Chlorinated hydrocarbons are harmful to the environment and toxic, and much effort is made to reduce the emission of these compounds. The destruction of chlorinated hydrocarbons into CO_2, H_2O and HCl can be performed by catalytic oxidation. The catalyst used must be active in the destruction of all kinds of chlorinated compounds, including

---

[*] Corresponding author. Fax: +31-71-5274451
E-mail address: jeurisse@chem.leidenuniv.nl (M.M.R. Feijen-Jeurissen)

[1] Co-corresponding author. Tel.: +33-388136973; fax: +33-388136975.

PII: S0920-5861(99)00169-8

toxic byproducts that can result from incomplete combustion.

Generally, two kinds of catalysts are used for this process: noble metals and metal oxides. Noble metals are very active catalysts for deep oxidation reactions, but they are known to be poisoned by chlorine and are susceptible to the formation of volatile metal oxychlorides. One of the most active metal oxide catalysts is chromium oxide. Although very active, application of this catalyst is restricted to low operation temperatures because the formation of volatile and very toxic chromium oxychloride can occur. Depending on the catalyst composition, both noble metal and metal oxide catalyst can also be active in the Deacon process and in oxychlorination reactions, which lead to the formation of molecular chlorine and undesired higher chlorinated compounds.

The oxidation of chlorinated methanes has been studied over many different catalysts. Al_2O_3 has been found to be active in the decomposition of CH_2Cl_2, leading to mainly CO and HCl. Experiments show that CH_3Cl, which is formally a reduction product, is formed too [1–4]. The mechanism of the decomposition of CH_2Cl_2 over γ-Al_2O_3 has been studied by FTIR-spectroscopy by van den Brink et al. [2] and Haber et al. [3]. The same absorption bands were observed but the interpretations of the spectra were different. Van den Brink et al. proposed that the mechanism involves the direct reaction of CH_2Cl_2 with surface hydroxyl groups resulting in adsorbed formaldehyde intermediates, which disproportionate into methoxy and formate species. Probably, Al–Cl bonds are formed during the reaction. Water can easily react with the Al–Cl bonds and regenerate the catalyst [2–4]. In this case, the destruction process is rather a hydrolysis than an oxidation.

The reaction of chloro-organics with Al_2O_3 is also described in the literature concerning the preparation of highly acidic chlorinated alumina catalysts. Chlorination is successfully performed by the reaction of chlorinated methanes containing at least two chlorine atoms. Methyl chloride and several chlorinated alkanes and alkenes are considered to be less reactive in chlorinating Al_2O_3 [5,6].

Although the oxidation of chlorinated C_2-hydrocarbons has also received attention, not much is known about the destruction mechanisms. In the case of chlorinated ethanes that contain a β-hydrogen HCl elimination is often observed and, consequently, the formation of more stable chlorinated ethylenes. Ramanathan et al. [7] performed 1,1-dichloroethane oxidation over a Cr_2O_3 on alumina catalyst. When the conversion started at 230°C, vinyl chloride was formed. At higher temperatures CO_x species, HCl and Cl_2 were observed. The sequential appearance of vinyl chloride and CO_x, HCl and Cl_2 product peaks suggests that dehydrochlorination is the first step in the oxidation of 1,1-dichloroethane. Similar results were obtained in the oxidation of 1,1,1-trichloroethane, where initial conversion into 1,1-dichloroethylene was found [7]. The decomposition of chlorinated alkanes was accompanied by a significant chlorine uptake in the catalyst [7,8]. Sinquin et al. [9] have studied the oxidation of 1,1,1-trichloroethane and 1,2-dichloroethane over $LaMnO_3$ perovskite catalysts. At room temperature 1,1,1-trichloroethane had already been partially converted into 1,1-dichloroethylene. Under dry and wet conditions, the complete dehydrochlorination into 1,1-dichloroethylene was reached at 90 and 170°C, respectively. At higher temperatures the formation of mainly trichloroethylene, tetrachloro-ethylene and CO_x was observed. The oxidation of 1,2-dichloroethane over $LaMnO_3$ started at about 300°C resulting in significant amounts of vinyl chloride. In addition, the production of $CHCl_3$, CCl_4 and 1,2-dichloroethylene was also observed. In the absence of water, carbon was retained by the catalyst at temperatures between 350 and 450°C, possibly due to the polymerisation of vinyl chloride on the catalyst surface [9].

The formation of vinyl chloride by dehydrochlorination was not observed by Imamura et al. and Lago et al. during the oxidation of 1,2-dichloroethane [8–10]. However, it is possible that at their relatively high reaction temperature ($T \geq 400$°C), any vinyl chloride formed had already been converted into other products. Imamura et al. performed the decomposition of 1,2-dichloroethane in air over several acid catalysts. At 400°C TiO_2/SiO_2 gave complete conversion into CO, CO_2 and HCl. Zeolites were less active and suffered from deactivation due to the formation of carbonaceous species [8]. Lago et al. used $CuCl/KCl/SiO_2$ as a catalyst for the oxidation of 1,2-dichloroethane. When the temperature is 450°C or higher, complete conversion into CO_x was observed. Below 450°C the chloride catalyst activated H–Cl exchange, and trichloroethane, tetrachloroethane and dichloroethylene were produced [10].

The elimination of HCl from chloroalkanes is promoted by solid bases and acid catalysts. A few studies have been published on the interaction between chloroethanes and Al_2O_3. The most extensive work has been conducted by Mochida and co-workers. Mochida [11] studied the dehydrochlorination of several chloroalkanes (including 1,1,2-trichloroethane, 1,2-dichloropropane and 1,1,2-dichloropropane) over alumina, base and acid catalysts under reductive reaction conditions. The HCl elimination reactions over dry alumina were postulated to proceed through an E_2-concerted mechanism, where the chlorine and hydrogen were eliminated almost simultaneously by the basic and acid sites of the alumina. During the reaction the alumina was chlorinated and it also deactivated. In the presence of water, alumina could be regenerated and a constant conversion could be maintained. Besides that, water influenced the selectivity. The change in the product distribution may come from a shift of the mechanism from E_2-concerted into E_1-cb. Dry alumina behaved more like acid catalysts, whereas the product distribution over hydrated alumina was more like that of a basic catalyst. Application of an excess of water may block the active sites. The extent of the shift in mechanism may depend on the acidity of the hydrogens to be eliminated as well as on the basicity of the catalyst. If the acidity of the hydrogen is strong enough the elimination may proceed via E_1-cb even though the basicity of the catalyst is not so strong. If the basic strength of the hydrated alumina is not high enough to eliminate the weakly acidic hydrogen the elimination of chlorine may not be ignored, leading to the E_2-concerted mechanism. Ballinger et al. [12] studied the interaction of 1,1,1-trichloroethane with Al_2O_3 by infrared spectroscopy. They found that at 300 K 1,1,1-trichloroethane was reversibly adsorbed via H-bridge bonding with isolated hydroxyl groups on the alumina surface. At 400 K 1,1-dichloroethylene was observed and at higher temperatures small amounts of carboxylates on the surface could be identified. The decomposition of 1,1,1-trichloroethane was faster over the more dehydroxylated Al_2O_3. Less 1,1-dichloroethylene and more intensive features due to carboxylates were observed for the higher dehydroxylated Al_2O_3. The just small effects on the OH-vibrations in the IR spectra during reaction made Ballinger et al. to conclude that the Al–OH groups are not involved in the main dehydrochlorination reaction of 1,1,1-trichloroethane. By that, the strong inhibition of 1,1,1-trichloroethane decomposition by pyridine, pre-adsorbed on the Al_2O_3 surface, would demonstrate the importance of Al^{3+} in this reaction. According to Ballinger et al. it is likely that the first step in 1,1,1-trichloroethane dehydrochlorination involves the abstraction of a chlorine ion from the parent molecule by an Al^{3+} site in a concerted fashion with proton abstraction.

The oxidation of chlorinated ethylenes has been examined over various catalysts. Generally, the reactivity of the chlorinated ethylenes decreases with increasing chlorine content in the molecule. The rate determining step probably does not involve breaking the C–Cl or C–H bonds. Bond et al. [13] suggested that over a Pt/Al_2O_3 catalyst the rate determining step is the removal of chlorine from the catalyst surface. Chintawar et al. extensively studied the oxidation of chlorinated ethylenes [14]. They found a strong correlation between the adsorption capacity of the molecule on the catalyst and the reactivity of the molecule. The activity of a chromium exchanged zeolite Y catalyst was ascribed to the high acidity of the catalyst, the high ionization potential of the chromium cation and the availability of multiple oxidation states [14]. The interaction of chlorinated ethylenes with the chromium exchanged zeolite Y was studied by FTIR. Based on these experiments it was postulated that the first step in the interaction of chlorinated ethylenes with the catalyst occurs through the abstraction of one or more chlorine atoms. The partially dechlorinated ethylene is then attacked by oxygen to yield carbonyl species which may or may not contain chlorine; for the destruction of vinyl chloride and trichloroethylene the formation of HCHO and $CHCl_2CHO$ was proposed, respectively. A following oxygen attack on the carbonyl compound results in the formation of carboxylate and carbonate species [15].

In this study the destruction mechanisms of C_2-chlorinated hydrocarbons have been investigated. The adsorption of 1,2-dichloroethane (DCE) on alumina and of trichloroethylene (TCE) on alumina and alumina supported catalysts has been studied at temperatures between room temperature and 300°C by infrared spectroscopy. In addition, the oxidation of

TCE over alumina supported palladium and chromium catalysts was examined.

2. Experimental

2.1. Catalysts and activity measurements

γ-Alumina (Degussa C, 100 m^2/g) supported catalysts containing 2 wt.% of Cr_2O_3 and 2 wt.% of Pd, respectively, were prepared by impregnation from aqueous solutions of chromium nitrate and palladium ammonium nitrate. After drying at 80°C overnight, calcination was carried out at 600°C for 3 h. The catalytic activity in the complete oxidation of trichloroethylene (TCE) was measured in a micro flow-reactor with gas streams containing 500 ppm TCE, 20% O_2 and 1% H_2O in nitrogen. In addition, preliminary experiments were performed on the destruction of 1,2-dichloroethane (DCE; 500 ppm) over γ-alumina. The experiments were performed in the temperature range from 50 to 500°C. At a GHSV of 10 000 h^{-1}, 0.3 g catalyst (150–300 μm) was used. The gas stream was analysed with an on-line gas chromatograph equipped with a CP-SIL5 column connected to a FID for the detection of organic molecules and a carbosphere column connected to a TCD for the detection of CO and CO_2. Characterisation could also be carried out by GC-MS. HCl and Cl_2 were not analyzed.

2.2. IR-spectroscopy

The adsorption of 1,2-dichloroethane (DCE) on γ-alumina (Rhone Poulenc, 206 m^2/g) and the adsorption of trichloroethylene (TCE) on γ-alumina (Degussa C, 100 m^2/g) and on the alumina supported catalysts was studied by IR spectroscopy in the temperature range from room temperature to 300°C. For the FTIR experiments a wafer of about 25–30 mg per 1 cm^2 was prepared. The sample was pretreated by heating overnight at 400°C in air to remove the hydrocarbons, followed by evacuation (10^{-5} mbar) at the same temperature for 2 h. After cooling to room temperature a spectrum was recorded of the catalyst. At reaction temperature the sample was subsequently exposed for one hour to about 2.5 mbar of TCE or DCE. The sample was moved to the IR cell where immediately a spectrum was recorded at room temperature in the presence of the gas phase and after evacuation. The spectra were recorded on a Nicolet 5 DXC spectrometer. The wavenumber range between 4000 and 400 cm^{-1} was scanned. Contributions to the gas phase, when present, have been removed by direct subtraction of the gas phase spectrum. TCE and DCE from Fluka (>99.5%) were used and dried with molecular sieve.

For peak identification comparable experiments have been performed with tetra-deuterated 1,2-dichloroethane (Aldrich 99 at.% D).

3. Results

3.1. Activity measurements: 1,2-dichloroethane

The destruction of DCE over alumina (Degussa C) has been examined under varying reaction conditions. The preliminary results show that, in an inert nitrogen flow and under oxidative reaction conditions, a large amount of vinyl chloride is formed at temperatures between 250 and 450°C. Almost complete conversion into vinyl chloride seems to be achieved around 350°C. The detection of acetylene at high temperature shows that a second HCl elimination occurs. Besides CO and CO_2 small amounts of not yet identified products have been detected too. In particular at high temperature, carbon is deposited on the catalyst surface. These results will be published later in detail.

3.2. Activity measurements: trichloroethylene

The activity of alumina and alumina supported chromium oxide and palladium catalysts has been examined for the complete oxidation of TCE. Contrary to the destruction of chlorinated methanes alumina is not very active in the conversion of TCE and reaction only occurs at temperatures above 400°C.

Fig. 1 shows the results for the destruction of TCE over alumina under varying reaction conditions. In the presence of only oxygen 85% conversion is initially reached at 500°C, but deactivation occurs. When the reaction is performed in the presence of both oxygen and water conversion proceeds at a slightly higher

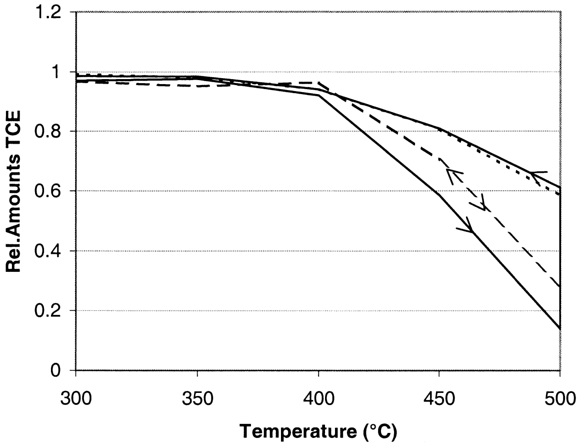


Fig. 1. TCE destruction over γ-Al_2O_3 in presence of: (—) O_2, (– –) O_2 and H_2O and (···) H_2O.

temperature than initially was found in the presence of oxygen alone. Deactivation has not been observed. Reaction in the presence of water without oxygen gives comparable conversion as seen in presence of only oxygen after deactivation. The products are CO and CO_2 under all three conditions. In the absence of oxygen carbonaceous species are formed at the surface, while the carbon balance is correct under oxidative conditions.

Palladium and chromium containing catalysts are more active. In Fig. 2 the results for the oxidation of TCE over a 2 wt.% Pd/Al_2O_3 catalyst in the absence and presence of water are shown. In the absence of H_2O 50 and 95% conversion are reached at 360 and 420°C, respectively. Besides CO_2 a significant amount of tetrachloroethylene (PCE) is formed, which is still present at 500°C, and some CO is observed between 250 and 400°C. Addition of water to the feed does not affect the conversion of TCE but results in an important decrease of the amount of PCE from 38% to about 4%. No significant amount of CO is detected under wet reaction conditions.

Fig. 3 shows the results for the oxidation of TCE over the 2 wt.% CrO_x/Al_2O_3 catalyst. In the presence of oxygen 50 and 95% conversion are reached at 260°C and about 290°C, respectively. CO, CO_2 and a small amount of PCE are formed. Addition of water to the feed results in a decreased conversion and prevention of PCE production.

3.3. IR spectroscopy

The adsorption of 1,2-dichloroethane (DCE) and of tetra-deuterated DCE on γ-Al_2O_3 has been studied between room temperature and 300°C. The gas phase spectrum of DCE and the absorption bands observed at DCE adsorption on alumina are summarised in Table 1. The spectra shown in the following figures were recorded in the presence of gas phase DCE unless stated otherwise.

Fig. 4 shows the C–H stretching frequency range for the adsorption of DCE on γ-Al_2O_3 at different temperatures. At room temperature (RT) an intense band

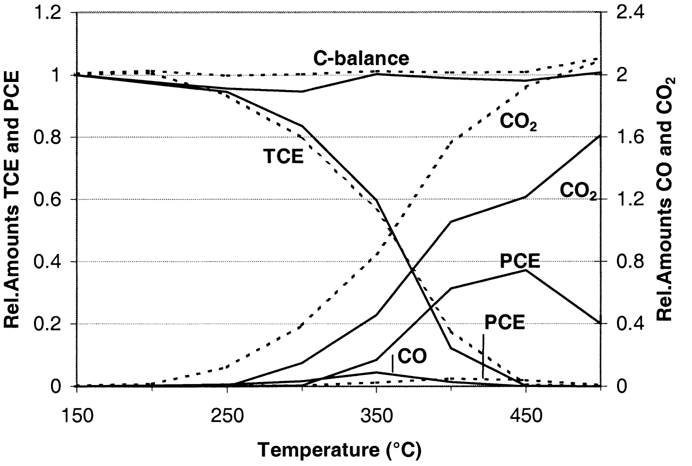


Fig. 2. TCE oxidation over 2 wt.% Pd/Al_2O_3 in: (—) absence and (···) presence of H_2O.

Table 1

Observed absorption bands for adsorption of 1,2-dichloroethane on γ-Al_2O_3 at room temperature, 100, 200 and 300°C compared to vinylchloride, acetaldehyde, acetate, acetic acid and acetyl species. Bold-italic characters refer to deuterated compounds

				Adsorbed DCE															
Vinyl chloride [15,16]		Gas phase DCE		RT	***RT***	100	***100***	200	***200***	300	***300***	Acetaldehyde [17]		Acetate [17,18]		Acetic Acid [19,20,21]		Acetyl [17,22]	
$\nu_a CH_2$	3130																		
	2337																		
$\nu_a CH_2$	3090																		
	2300				***2270***		***2267***												
$\nu_s CH_2$	3040			3030															
	2225				***2222***				***2214***		***2217***								
									2232		***2238***			$\nu_a CH_3$	3023	$\nu_a CH_3$	3026		***2232***
				3008								$\nu_a CH_3$	3008						
					2252								***2256***						
		$\nu_a CH_2$	2987			2988								$\nu_a CH_3$	2989				
		+ rot	***2190***		***2202***										***2264***				
		$\nu_a CH_2$	2976			2976													
		+ rot	***2179***		***2177***		***2177***		***2176***										
				2965		2963		2965										$\nu_a CH_3$	2965
							2185												***2175***
		$\nu_s CH_2$	2957					2941				$\nu_s CH_3$	2957	$\nu_s CH_3$	2940				
		+ rot			***2137***				***2117***				***2135***		***2111***				
		$\nu_s CH_2$	2898																
		+ rot	***2100***																
			2888	2883															
				2849								νCH	2842						
													2047						
												$\nu C=O$	1752			$\nu C=O$	1792		
												+rot	1737			+rot	1786		
													1749				1734		
													1732				***1780***		
													1722						
						1688		1686		1690		$\nu C=O$	1696			$\nu C=O$	1698	$\nu C=O$	1664
						1644		1634		1642		ads				ads			
					1694		***1669***		***1681***		***1668***		***1696***				***1690***		*1673*
					1684		***1653***		***1652***										
							1624		***1620***		***1623***								
$\nu C=C$	1605						***1603***												
	1599					1594		1589		1587									
	1537				***1552***		***1555***		***1560***		***1555***								
				1575		1575		1574		1576				$\nu_a COO$	1578				
							1585		***1584***		***1579***				***1545***				

Table 1 (*Continuned*)

				Adsorbed DCE															
Vinyl chloride [15,16]		Gas phase DCE		RT	***RT***	100	***100***	200	***200***	300	***300***	Acetaldehyde [17]		Acetate [17,18]		Acetic Acid [19,20,21]		Acetyl [17,22]	
				1552		1554		1548											
					1521		***1521***												
						1467	***1460***	1466	***1465***	1467	***1465***								
									1353		***1351***								
		δ_aCH$_2$	1465	1466		1467		1466		1467					1498				
		+rot	***1150***		***1150***		***1151***		***1150***				***1151***						
		δ_aCH$_2$	1453	1450		1453						δ_aCH$_3$	1446	δ_aCH$_3$	1443				
		+rot	***1140***		***1135***								***1029***		***1047***				
			1432	1432		1432		1430		1432						δCH$_3$	1428		
					1060		***1060***		***1062***		***1056***					dimer	***1052***		
						1400		1397		1395				δCH$_3$	1414	δCH$_3$	1408		
										1380							1395		
					1078		***1077***		***1079***		***1081***				***1046***		***1079***		
δCH$_2$	1387			1383															
+ rot	1361					1360		1360		1360			1347		1343				
				1315		1315		1315		1315									1314
					1123		***1123***												***1123***
		δ_sCH$_2$	1299																
		+ rot	***1019***																
ρCH	1290	δ_sCH$_2$	1288	1288		1288		1285		1285						νCOO	1290		
		+ rot	***1015***		***1014***		***1014***		***1012***		***1016***					dimer	***1291***		
ρCH	1269			1260				1273											
	1044			1260				1273											
		ρCH$_2$	1238	1237		1236		1235		1236									
			947																
			1228																
			935																
					1189	1189	***1183***	1189	1182							ν_sCOO	1178		
					1255		***1170***										***1298***		
				1150															
						1101		1101		1100		ν_aC–C	1108						
													1046						
				1070		1072		1075		1079						ρCH	1075		
																dimer			
ρCH$_2$	1023			1033															

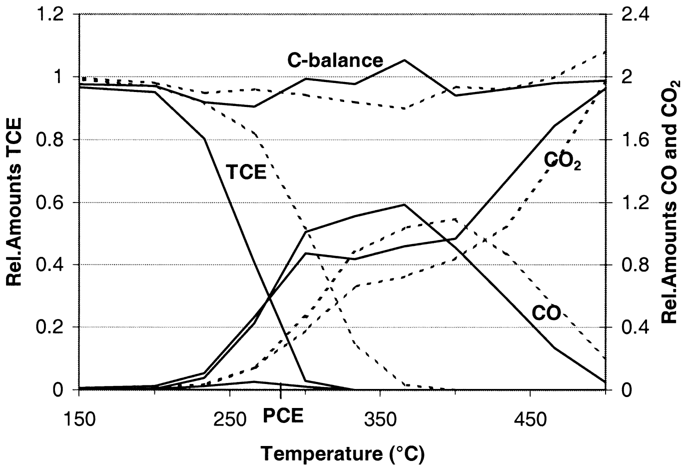


Fig. 3. TCE oxidation over 2 wt.% CrO_x/Al_2O_3 in (—) absence and (···) presence of H_2O.

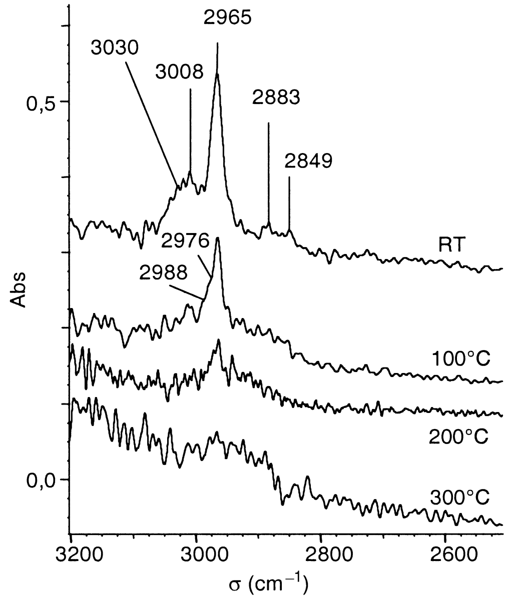


Fig. 4. C–H stretch vibrations for adsorption of DCE on γ-Al_2O_3 at room temperature, 100, 200 and 300°C.

at 2965 cm^{-1}, a broad band around 3030–3008 cm^{-1} and weak vibrations at 2883 and 2849 cm^{-1} are observed, indicating that several types of C–H bonds are present. When adsorption is performed at higher temperatures the peak intensities decrease. At 100°C the peak at 2965 cm^{-1} has shoulders at 2976 and 2988 cm^{-1}. Although they are difficult to observe, due to a low signal–noise ratio, very weak absorptions between 2980 and 2845 cm^{-1} seem to be present at 100, 200 and 300°C.

Fig. 5 shows the frequency range between 1800 and 1000 cm^{-1} for the adsorption of DCE on γ-Al_2O_3. Due to strong Al–O vibrations, absorption bands below 1000 cm^{-1} are not visible, and therefore, C–Cl bonds cannot be identified. At room temperature intense bands at 1552, 1450, 1432, 1315, 1288, 1236 and 1033 cm^{-1} are observed. In addition, a weak band at 1150 cm^{-1}, a shoulder around 1271 cm^{-1} and a broad weak vibration at 1070 cm^{-1} are observed. Adsorption at increasing temperature gives additional bands at 1688, 1644, 1594, 1575, 1467, 1400, 1380, 1360 and 1189 cm^{-1}. Generally, evacuation results in the disappearance of the peaks at 1288 and 1236 cm^{-1} and in a decrease in the intensity of the bands at 1450, 1435 and 1315 cm^{-1}.

For identification of the observed vibrations, similar experiments have been carried out with tetradeuterated 1,2-dichloroethane (DCE-i). Figs. 6 and 7 show the spectra obtained for the adsorption of DCE-i on γ-Al_2O_3 at room temperature, 100, 300 and 400°C.

Pertubations around ~2300–2400 cm^{-1} are no real product peaks, but the result of the changing CO_2 background. At room temperature C–D stretch vibrations are observed at 2270, 2252, 2222, 2202, 2177 and 2137 cm^{-1}. At 100°C only the bands at 2267 and 2177 cm^{-1} are still present and a weak new band at 2185 cm^{-1} appears. These bands are not present

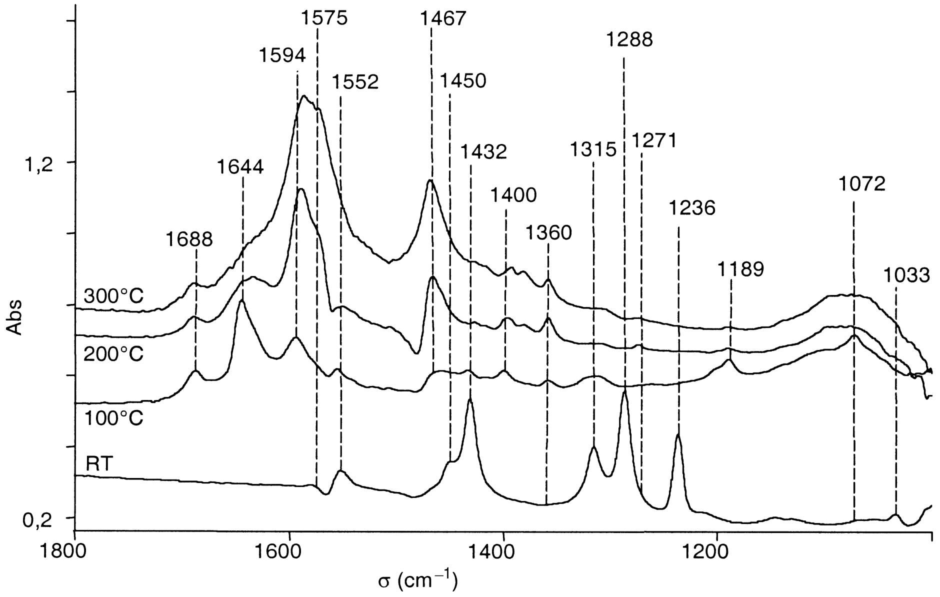


Fig. 5. Adsorption of DCE on γ-Al_2O_3 at room temperature, 100, 200 and 300°C.

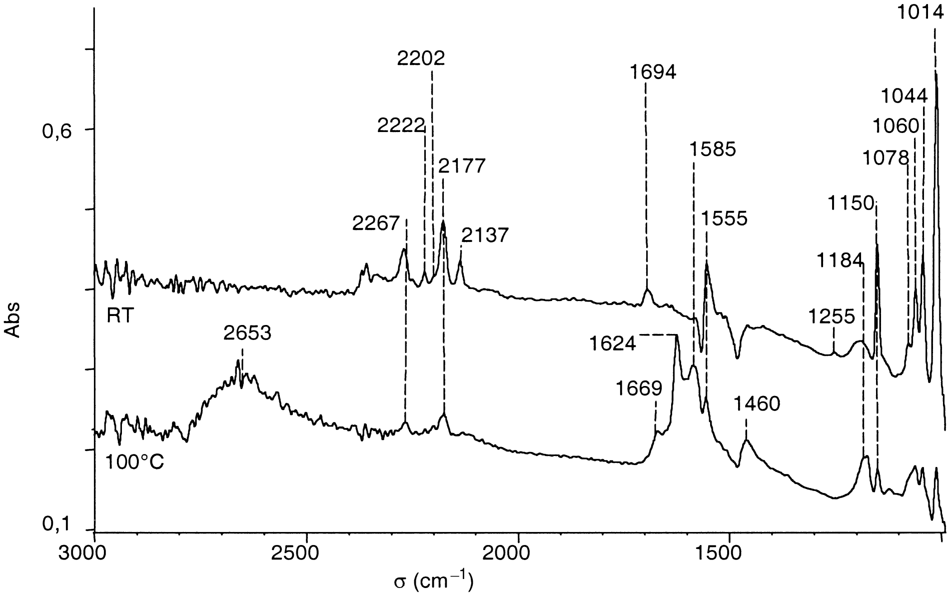


Fig. 6. Adsorption of DCE-i on γ-Al_2O_3 at room temperature and 100°C.

at higher temperatures, where contributions at 2238, 2217 and 2117 cm^{-1} can be seen.

In the range from 1700 to 1000 cm^{-1} many different absorption bands are present. At room temperature intense absorption bands are observed at 1694, 1552, 1189, 1150, 1078, 1060, 1044 and 1014 cm^{-1} and another at 1255 cm^{-1}. For adsorption at higher temperatures the bands between 1000 and 1100 cm^{-1} become less pronounced and are finally replaced by a broad band around 1081 cm^{-1}. Those at 1150, 1694

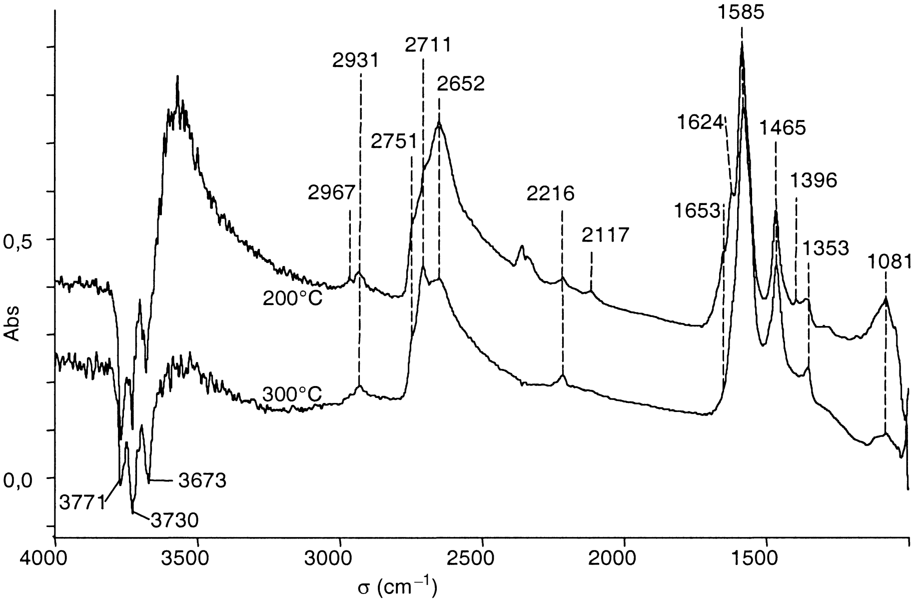


Fig. 7. Adsorption of DCE-i on γ-Al_2O_3 at 200 and 300°C; recorded after evacuation.

and 1255 cm^{-1} decrease with increasing temperature and disappear. New bands are observed at 1669, 1653, 1624, 1396 and 1353 cm^{-1}. Besides that two bands at 1585 and 1465 cm^{-1} become very strong with increasing temperature.

Due to adsorption of DCE the gas phase does not change significantly, except for reaction at 300°C. Fig. 8 shows the change in gas phase after adsorption of DCE and DCE-i on γ-Al_2O_3 at 300°C. It can be clearly seen that these spectra contain absorption bands which can be ascribed to vinyl chloride. During the adsorption experiments at elevated temperatures the white alumina disk became brown-black.

The same experiments have been undertaken for the adsorption of trichloroethylene on γ-Al_2O_3 and on the alumina supported palladium and chromium catalysts. The attribution of the absorption bands is more difficult and will be published in detail elsewhere [23].

4. Discussion

The spectra of 1,2-dichloroethane and tetradeuterated 1,2-dichloroethane, adsorbed on γ-Al_2O_3, are rather complicated and difficult to interpret. However, with the help of deuterated products a tentative interpretation can be made. The observed absorption bands of gas phase 1,2-dichloroethane and of 1,2-dichloroethane adsorbed on γ-Al_2O_3 are summarized in Table 1. In addition, the band assignment is mentioned. The bold-italic characters refer to the bands observed for the deuterated compounds.

Adsorption was performed at temperatures between room temperature and 300°C. At room temperature, it can be clearly seen that adsorbed vinyl chloride is formed. ($\nu_s CH_2$: 3030 cm^{-1}, ρCH: 1288 and 1260 cm^{-1}, ρCH_2: 1033 cm^{-1}, $\nu_a CD_2$: 2270 cm^{-1}, $\nu_s CD_2$: 2222 cm^{-1}, νC=C: 1552 cm^{-1} and ρCD: 1044 cm^{-1}). The activity measurements showed that over alumina DCE is easily converted into vinyl chloride. The formation of vinyl chloride by dehydrochlorination of 1,2-dichloroethane in the presence of Lewis acids, like $AlCl_3$, is well known [24]. Dehydrochlorination of 1,2-dichloroethane has also been shown to be the first step in the catalytic oxidation over perovskite catalysts [9]. Generally, HCl elimination from chloroalkanes can be promoted by solid bases and acid catalysts. Dehydrochlorination of many chloroalkanes has been observed over alumina; the mechanism is found to depend a.o. on the degree of dehydroxylation of the alumina surface [11,12].

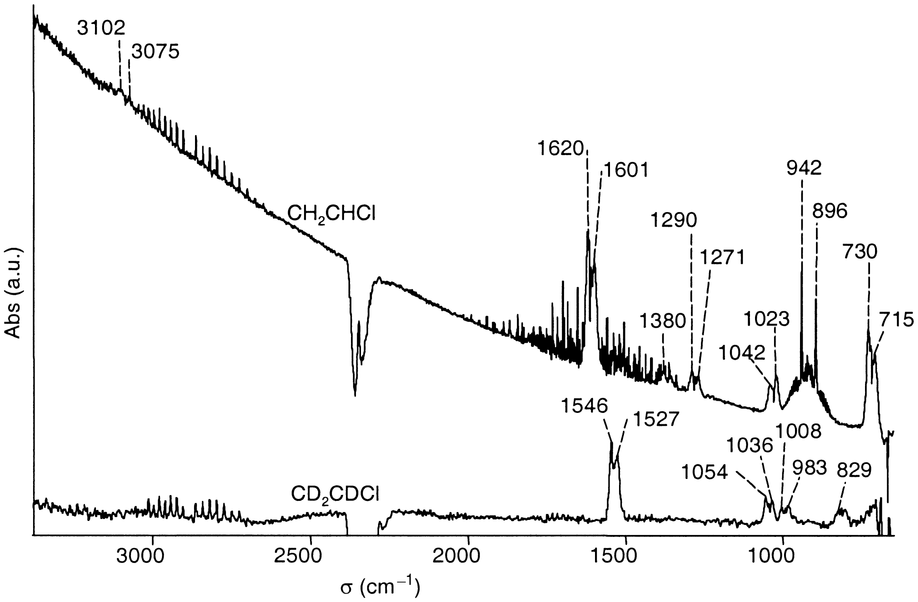
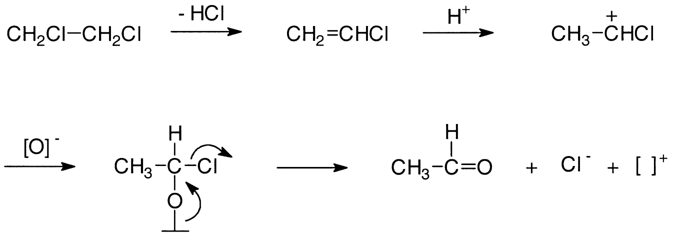


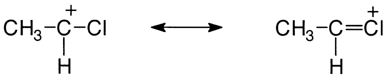
Fig. 8. Change in gas phase due to adsorption of DCE and DCE-i on γ-Al_2O_3 at 300°C.



Scheme 1.

The second species formed is an adsorbed acetaldehyde corresponding to a coordination to a Lewis acid, R–C^H=O- -Al^{3+} ($\nu_a CH_3$: 3008 cm^{-1}, νCH: 2849 cm^{-1}, νC=O: 1684 cm^{-1}, $\delta_a CH_3$: 1446 cm^{-1} and ν_aC–C: 1108 cm^{-1}). Chintawar et al. observed for the adsorption of vinyl chloride on a chromium exchanged zeolite Y a band at 1678 cm^{-1} and assigned this band to an adsorbed aldehyde or ketone [15]. With respect to the deuterated compound the fit for carbon–hydrogen vibration is somewhat less good, possibly, because the carbon–hydrogen groups contain both hydrogen and deuterium. The νC=O (1696 cm^{-1}), however, is consistent with an adsorbed acetaldehyde. The presence of vibration bands of CH_3 show that a chlorine from the parent CH_2Cl–CH_2Cl is replaced by a hydrogen atom. The formation of acetaldehyde could be ascribed to Scheme 1.

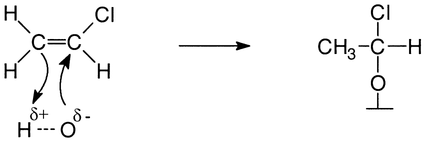
Vinyl chloride can readily be protonated in the presence of acid catalysts, like $AlCl_3$, in the presence of moisture or OH surface species [24]. By the protonation a reactive carbonium ion is formed that is stabilized by resonance (Scheme 2).



$$CH_3-\underset{H}{\overset{+}{C}}-Cl \longleftrightarrow CH_3-\underset{H}{C}=\overset{+}{Cl}$$

Scheme 2.

The attack on the carbocation by a nucleophilic oxygen species (basic site of alumina or adsorbed water) would lead to the CH_3–CHCl – O – species, which would readily decompose to form acetaldehyde and leaving a chloride ion on the surface. The attack of a C–Cl bond by basic sites on metal-exchanged zeolites have been shown by Murray et al., and Krawietz for various chloromethanes [25,26]. An alternative for the intermediate formation of a carbocation is the simultaneous attack of both carbon atoms of vinyl chloride by an OH group according to the following scheme (Scheme 3):



Scheme 3.

At 100°C, some bands indicate the presence of adsorbed acetic acid as a dimer: νC=O: 1698 cm^{-1}, δCH_3: 1408 cm^{-1}, νCOO: 1290 cm^{-1}. This is not unexpected since acetaldehyde is known to be easily oxidised into acetic acid. The band at 1290 cm^{-1} is shifted slightly for the deuterated compound to 1255 cm^{-1}.

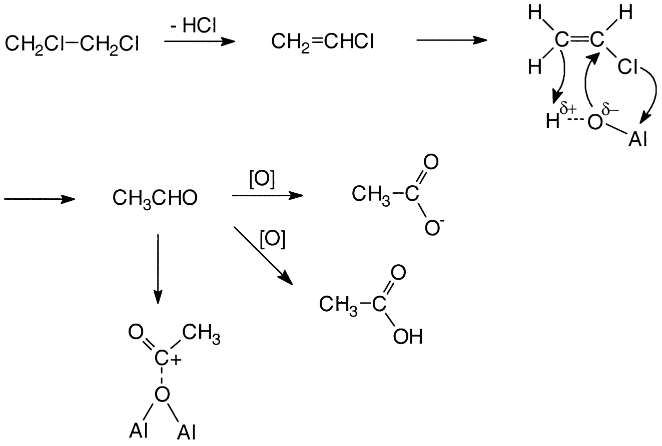
At 100 and 200°C bands appear which could correspond to an acetyl species: $\nu_s CH_3$: 2965 cm^{-1}, νD_2H: 2175 cm^{-1}, ν_sC=O: 1664 cm^{-1} and a band at 1314 cm^{-1} which was found to be characteristic of an acetyl species. Finally, at higher temperatures (300°C) only bands corresponding to an acetate species (see Table 1) and monodentate bonded carbonates (1465 and 1353 cm^{-1}) [27], were observed. Scheme 4 would explain the observed species and be in agreement with the known chemistry. It is not completely clear in which order the addition of the hydrogen and oxygen and the elimination of the chlorine take place. Based on organic chemistry the attack by the hydrogen on the vinyl chloride is likely to be the first step.

The same experiments have been undertaken for the adsorption of trichloroethylene. The attribution of the bands is more difficult and will be published in detail elsewhere [23]. Adsorption of trichloroethylene on γ-Al_2O_3 at room temperature showed that only a physical adsorbed species is observed. The difference with gas phase trichloroethylene is that the bands due to rotation disappear in the adsorbed species. At higher temperatures (200–300°C) the bands characteristic of a monodentate monochloroacetate could be evidenced by comparison with the bands of sodium chloroacetate ($\nu_s CH_2$: 2956 cm^{-1}, ν_aC=O: 1603 cm^{-1}, ν_sC=O: 1456 cm^{-1}, CH_2 bend: 1414 cm^{-1}, CH_2 twist: 1261 cm^{-1}, ρCH_2: 1156 cm^{-1}). Indications of the formation of monochloroacetate are also observed for the adsorption of TCE on the alumina supported palladium catalyst.

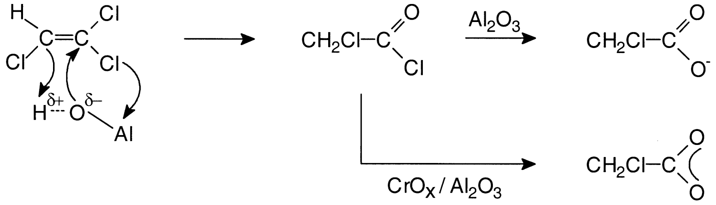
On CrO_x/Al_2O_3 an additional band is observed at 1755 cm^{-1}. Such a feature was also observed by Chintawar et al. [15] for the adsorption of trichloroethylene on Cr exchanged zeolite Y (1751 cm^{-1}). They attributed this band to $CHCl_2CHO$ by comparison with the work of Philipps and Raupp [28]. However, Philipps and Raupp worked in the condition of photochemistry. The formation of $CHCl_2CHO$ would imply an anti-Markovnikov addition to trichloroethylene which is likely in photochemistry. But under our conditions a Markovnikov attack would be more likely. Our results concerning the adsorption of monochloroacetyl chloride on alumina suggests rather an adsorbed monochloroacetyl chloride species of the type CH_2Cl–C^{Cl}=O- -Al^{3+}. Such species are known in the reaction of acylchloride with protic acids [24]. The bands which can be attributed to a monochloroacetate, are shifted compared to γ-Al_2O_3 and suggest the formation of a bidentate structure. On the chromium catalyst, CH_2Cl–COCl seems to be stabilized compared to γ-Al_2O_3. Further a band at 1617 cm^{-1} together with one at 1250 cm^{-1} appears already at room temperature and does not correspond to an adsorbed water molecule but rather to a carbonate species, showing that destruction is already working at room temperature with the chromium containing catalyst. A proposed mechanism of trichloroethylene oxidation is shown in Scheme 5.

It is not known in which order the attack of hydrogen and oxygen and the elimination of chlorine occur. Based on organic chemistry the attack by the oxygen on TCE is likely to be the first step.

Acid halides are readily hydrolysed, the lower ones such as acetyl chloride react violently with water resulting in acidic acid [29]. When acyl chlorides are heated in the presence of $AlCl_3$, they decompose with the liberation of CO and the corresponding alkylchlorides [24]. Electron-donating substituents in the acid residue accelerate the elimination of CO and electron-withdrawing substituents retard it. When monochloroacetyl chloride is heated in the presence



Scheme 4.



Scheme 5.

of $AlCl_3$ evolution of CO, HCl and chloroacetylene and formation of a polymeric product were observed. The decomposition of monochloroacyl chloride probably takes place through CO elimination and formation of dichloromethane. The formation of HCl and chloroacetylene is due to secondary conversions of CH_2Cl_2 [24]. The decomposition of chloroacetyl chloride on CrO_x/Al_2O_3 with formation of CO_2 at room temperature could explain the formation of carbonates, since CO can be oxidized into CO_2 by CrO_x.

Due to strong Al–O bonds alumina is not a good oxygen donating agent, which explains the low activity of alumina for the oxidation of TCE. When HCl is present the Al–O bond possibly breaks more easily. Besides, impurities present in the alumina might change the properties and by that the activity of alumina. Another reason for the low activity of alumina is that acetates adsorbed on γ-Al_2O_3 are very stable. On the basis of the proposed reaction scheme the activity of the chromia and the palladium catalysts might be the result of the capability to supply oxygen which can attack the double bond. The inhibitive effect of water on the conversion of TCE over the chromia catalyst, is probably due to blocking of active oxygen sites. The less strong adsorption of water on the palladium surface would explain why the inhibitive effect is not found for the palladium catalyst.

The formed byproduct, tetrachloroethylene, in the presence of noble metals and metal oxides could be explained by chlorination followed by dehydrochlorination as follows (Schemes 6 and 7):

$$CCl_2{=}CHCl \xrightarrow[M\text{-}Cl]{Cl_2 \text{ or}} CCl_3{-}CHCl_2 \xrightarrow{-\,HCl} CCl_2{=}CCl_2$$

Scheme 6.

$$2\,HCl + 1/2\,O_2 \rightleftharpoons Cl_2 + H_2O$$

Scheme 7.

As TCE contains more chlorine atoms than hydrogen atoms, Cl_2 is formed in the absence of water. By the addition of water to the feed, an extra hydrogen source is supplied for the HCl formation. Moreover water can cause the removal of chlorine species from the catalyst surface, and if under the reaction conditions the Deacon equilibrium is reached, the addition of water to the feed reduces the amount of Cl_2 by the reverse Deacon reaction. (Reduction from 206 to 102 ppm Cl_2, from 615 to 267 ppm Cl_2 and from 584 to 135 ppm Cl_2 at 327, 427 and 527°C, respectively) [30]. Less molecular chlorine and chlorine on the catalyst surface will result in a reduced formation of tetrachloroethylene.

5. Conclusions

The adsorption of 1,2-dichloroethane (DCE) on γ-Al_2O_3 has been studied by IR in the temperature range from room temperature to 300°C. The spectra show the presence of vinyl chloride and indicate the presence of adsorbed acetaldehyde coordinated to a Lewis acid site and adsorbed acetic acid. In addition, some bands characteristic of acetyl species were observed. On the basis of these results it is suggested that the destruction of DCE occurs via HCl elimination to vinyl chloride. A subsequent attack of a hydrogen and a surface oxygen on the double bond of vinylchloride results in the formation of adsorbed acetyl chloride. Elimination of a chloride ion gives acetaldehyde that can be further oxidized into acetates.

The activity of alumina and alumina supported catalysts for the oxidation of trichloroethylene (TCE) has been studied by flow experiments, and the interaction of TCE with the catalysts by IR spectroscopy. Contrary to the destruction of chlorinated methanes alumina is not active in the oxidation of TCE. Active catalysts are alumina supported chromia and palladium catalysts. Over the palladium catalyst significant amounts of tetrachloroethylene (PCE) are produced in the absence of water. Addition of water to the feed decreases the amount of PCE for the palladium catalyst from 38 to 4%, whereas it does not influence the conversion of TCE. Over the chromia catalyst a small amount of PCE is formed under dry circumstances. Addition of water to the feed prevents the formation of PCE, and besides that, it inhibits the oxidation reaction over CrO_x.

Based on IR experiments the following reaction scheme has been proposed: TCE is attacked by a basic oxygen and a hydrogen according to Markovnikov's rule. This results in the formation of acyl chloride, which is further converted into acetate like species.

Due to strong Al–O bonds alumina is not a good oxygen donating agent, what explains the low activity of alumina for the destruction of TCE. In the presence of HCl, the alumina bonded oxygen can possibly leave more easily. The presence of impurities in the alumina might change the properties of alumina and by that the activity. Another reason for the low activity of alumina is that acetates adsorbed on γ-Al_2O_3 are very stable. The activity of the chromia catalyst might be the result of the capability to supply basic oxygen which can attack the double bond. The inhibitive effect of water on the conversion of TCE is probably due to blocking of active oxygen sites.

Acknowledgements

This work has been performed by M.M.R. Feijen-Jeurissen, partly at the LERSCI in Strasbourg, and was possible by a grant of the Netherlands Organization for Scientific Research (NWO). The authors wish to thank Professor Alain Kiennemann for the hospitality and R. van den Brink for his contribution. The work is part of a research program in the European Union Framework Climate and Environment, contract number EV5V-CT94-0530. The work has been performed under auspices of NIOK, the Netherlands Institute for Catalysis Research, Lab. Report #UL 99-2-06.

References

[1] G.C. Bond, F. Rosa, Calzadilla, Catal. Lett. 39 (1996) 261.
[2] R.W. van den Brink, P. Mulder, R. Louw, G. Sinquin, C. Petit, J.P. Hindermann, J. Catal. 180 (1998) 153–160.
[3] J. Haber, T. Machej, M. Derewinski, R. Janik, J. Krysciak, H. Sadowska, Z. Phys. Chem. 197 (1996) 97.
[4] M.M.R. Feijen-Jeurissen, E.C. van Winden, B.E. Nieuwenhuys, in preparation.
[5] G. Clet, J.M. Goupil, D. Cornet, Bull. Soc. Chim. Fr. 134 (1997) 223.
[6] A.G. Goble, P.A. Lawrance, in: Proc. 3rd Int. Cong. Catal., vol. I, North Holland, Amsterdam, 1964, p. 320.
[7] K. Ramanathan, J.J. Spivey, Combust. Sci. Tech. 63 (1989) 247.
[8] S. Imamura, H. Tarumoto, S. Ishida, Ind. Eng. Chem. Res. 28 (1989) 1449.

[9] G. Sinquin, J.P. Hindermann, C. Petit, A. Kiennemann, to be published.
[10] R.M. Lago, M.L.H. Greene, S.C. Tsang, M. Odlyka, Appl. Catal. B, Environ. 8 (1996) 107.
[11] I. Mochida, A. Uchino, H. Fujitsu, K. Takeshita, J. Catal. 51 (1978) 72.
[12] T.H. Ballinger, J.T. Yates Jr., J. Phys. Chem. 96 (1992) 1417.
[13] G.C. Bond, N. Sadeghi, J. Appl. Chem. Biotechnol. 25 (1975) 241.
[14] P.S. Chintawar, H.L. Greene, Appl. Catal. B, Environ. 13 (1997) 81.
[15] P.S. Chintawar, H.L. Greene, J. Catal. 165 (1997) 12.
[16] S. Enomoto, M. Asahina, J. Mol. Spectroscop. 19 (1966) 117.
[17] D. Demri, J.P. Hindermann, C. Diagne, A. Kiennemann, J. Chem. Soc. Faraday Trans. 90 (1994) 501.
[18] K. Ito, H.J. Bernstein, Can. J. Chem. 34 (1956) 170.
[19] M.A. Henderson, Y. Zhou, J.M. White, J. Am. Chem. Soc. 111 (1989) 1185.
[20] W. Hieber, G. Braun, W. Beck, Chem. Ber. 93 (1960) 901.
[21] D.M. Adams, G. Booth, J. Chem. Soc. (1962) 1112.
[22] Y. Maréchal, J. Chem. Phys. 87 (1987) 6344.
[23] M.M.R. Feijen-Jeurissen, J. Nienhuis, B.E. Nieuwenhuys, G. Sinquin, C. Petit, J.P. Hindermann, in preparation.
[24] A.E. Kulikova, E.N. Zil'berman, Russian Chem. Rev. 40 (1971) 256.
[25] D.K. Murray, J.W. Chang, J.F. Haw, J. Am. Chem. Soc. 115 (1993) 4732.
[26] T.R. Krawietz, P.W. Goguen, J.F. Haw, Catal. Lett. 42 (1996) 41.
[27] M.L. Hair, Infrared Spectroscopy in Surface Chemistry, Marcel Dekker, New York, 1967, p. 205–208.
[28] L.A. Phillips, G.B. Raupp, J. Mol. Catal. 77 (1992) 297.
[29] J. McMurry, Organic Chemistry, 2nd ed., Brooks/Cole Publ. Company, California, 1988, p. 752.
[30] D.R. Stull, H. Prophet, J. Chao, A.T. Hu, E.W. Philips, S.K. Wollert, S. Levine, J.L. Curnutt, JANAF Thermochemical Tables, 2nd ed., NSRDSNBS-37, National Bureau of Standards, Washington, 1971.