Hydrolytic decomposition of dichlorodifluoromethane on modified zirconium oxide surfaces

A. Hess and E. Kemnitz*

Institut für Chemie der Humboldt-Universität zu Berlin, Hessische Strasse 1/2, D-10115 Berlin, Germany

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The hydrolytic decomposition of dichlorodifluoromethane (CFC-12) on various modified zirconium oxide surfaces has been studied. The reaction was carried out under flow conditions at 500°C. Complete CFC-12 conversion and long-time stability of the catalysts were achieved accompanied by a limitation of the undesired CFC-13 formation. A maximum CFC-12 conversion was observed on catalysts of sulfated zirconia or zirconia obtained from temperature-controlled calcination of zirconium oxide hydrate. The reaction depends on the presence or in situ formation of Brønsted acid sites. FTIR-photoacoustic measurements were performed on pyridine complexes chemisorbed on the catalyst surface in order to analyze the changes in the catalyst's acidity. The effects of the temperature and water in the reaction gas on the catalyzed decomposition of CFC-12 are examined.

Keywords: decomposition, hydrolysis, heterogeneous catalysis, dichlorodifluoromethane, CFC-12, zirconia

1. Introduction

Chlorofluorocarbons (CFCs) are considered to be responsible for the stratospheric ozone depletion. Although their world-wide replacement is in progress there are enormous quantities of CFCs still in use. To prevent the release of CFCs a safe disposal and subsequent decomposition is necessary. Besides the energy-intensive incineration there is another route of decomposition – the heterogeneously catalyzed hydrolysis of the CFCs on metal oxide surfaces. The latter process occurs at significantly lower temperatures producing carbon dioxide, hydrogen fluoride and hydrogen chloride. Much effort has gone into searching for appropriate catalysts since 1992. Imamura et al. [1] have investigated various acid catalysts such as zeolite, silica–alumina and titania–silica. The latter showed the highest activity in decomposing dichlorodifluoromethane (CFC-12), but a rapid deactivation occurred due to the formation of volatile fluorides. The period of high catalytic activity was prolonged by adding water to the reaction gas [2]. The authors have characterized the following catalysts in detail: titania–silica, phosphate-supported zirconia and boron phosphate. Since no deactivation of the boron phosphate catalyst was observed during long-term operation, it was recommended for practical application. Phosphated zirconia exhibited a long period of catalytic activity, too [3,4]. Using this catalyst, CFC-12 in a mixture of 0.6% CFC-12, 21.2% O_2, 77.2% He and 1% water was completely decomposed at a minimum temperature of 300°C. The formation of small amounts of ZrF_4 as well as the decrease in acid strength was discussed to be the reason for the activity reduction after long-time operation. Karmakar et al. [5] have tested titania as a catalyst for CFC-12 decomposition in the presence of water vapour. They found a CFC-12 conversion $> 90\%$ at 300°C with a comparatively low long-term deactivation. The observed catalyst surface area reduction was accompanied by an increase in surface acidity. Their proposed mechanism comprises an adsorption of the CFC on the surface hydroxyls, further reaction between them and at least the formation of CO_2 with COFCl and $COCl_2$ as intermediates. Recently, we have published the results of a γ-alumina catalyst with special regard to the minimization of undesired side reactions as CFC-12 disproportionation and CFC-12 fluorination [6]. However, it was not possible to clarify whether the by-product chlorotrifluoromethane (CFC-13) originated from disproportionation or fluorination.

In this present paper, the hydrolytic decomposition of CFC-12 on modified zirconia catalysts including superacid sulfated zirconia is studied. The reaction parameters are optimized to increase the degree of CFC-12 conversion and to reduce the amount of by-products. The role of Brønsted and Lewis acid sites is discussed.

2. Experimental

2.1. Catalyst preparation

The catalyst precursor zirconium dioxide hydrate was prepared by hydrolyzing $ZrOCl_2{\cdot}xH_2O$ (A) or $ZrO(NO_3)_2$ (B) with aqueous ammonia until a pH of 8 was achieved. The precipitate was washed with water and calcined overnight at 110°C (precursors A and B). Precursor C was a zirconia aerogel obtained by precipitation from tetrabutoxyzirconium(IV) in butanol and

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* To whom correspondence should be addressed.

subsequent treatment in an autoclave according to ref. [7]. Table 1 lists all samples including their further modification.

2.2. Catalytic hydrolysis

The heterogeneously catalyzed hydrolysis of CFC-12 was performed under normal pressure using a gas flow reaction apparatus as described elsewhere [6]. The flow reactor (nickel, length 400 mm, inner diameter 5 mm) was heated using a controllable electric furnace. The catalyst powder was pressed into pellets, subsequently crushed and sieved to obtain particle diameters of 250–500 μm. For each reaction, 750 mg of the catalyst were charged in the reactor on a nickel sieve. At the beginning, the catalyst was calcined at 500°C in a pre-dried nitrogen gas flow (flow rate: 19.8 ml/min) for 1 h. After calcination, the reaction temperature was adjusted and a constant gas flow containing CFC-12, water vapour and nitrogen was allowed to pass through the catalyst. The nitrogen and CFC-12 gas flow were kept constant by a gas flow controller (MKS Instruments). The constant nitrogen stream was passed through a thermostated saturator with distilled water. Then, CFC-12 and nitrogen/water were mixed and introduced into the reactor. The composition of the gas flow was: 19.8 ml/min N_2; 3.24 ml/min CFC-12; molar ratio CFC-12/H_2O = 1/2.4.

The residence time t_r (3 s) was estimated by subdividing the free volume of the catalyst bed by the gas flow of all components. The analysis of gaseous products (CFCs and CO_2) was performed by GC as described previously [6]. Hydrogen fluoride and chloride were determined by absorption in 1 m NaOH for 2.5 min and were titrated using 0.5 m H_2SO_4. The concentrations of fluoride and chloride were determined by ion-sensitive electrodes.

2.3. Characterization of the catalysts

The catalysts were characterized before and after reaction by the following methods. XRD was performed using a XRD 7 Seiffert-FPM (Cu K_α). The specific surface areas of the samples were determined by the standard BET method of nitrogen adsorption using an ASAP 2000 system (Micromeritics, maximum experimental error ±1%). The Cl and S contents were obtained from elemental analysis. The analysis of the fluoride contents was performed as described previously [8].

2.4. Determination of surface acidity

The nature of acid sites was determined by FTIR photoacoustic spectroscopy of pyridine chemisorbed on the catalyst surface (70 mg) at 150°C under flow conditions. During the experiment a constant flow of 0.5 ℓ/h dried N_2 was employed. The pyridine feed was carried out in the following way. Liquid pyridine (30 μl) was injected into a vaporizer (150°C) located just before the inlet of the flow reactor. The excess gaseous and physisorbed pyridine was removed by holding the temperature for 15 min under the controlled N_2 flow. After cooling down to room temperature, 64 scans were recorded using a MTECH photoacoustic cell in combination with a Perkin-Elmer FTIR system 2000. The sample was purged for 10 min with dried helium. Further details are given elsewhere [9].

For a semiquantitative evaluation of the acid centers, the measured intensities from FTIR-spectra were con-

Table 1
Catalyst preparation

Sample notation	Precursor	Sample impregnation/modification	Final calcination
ZrO_2/comm1	–	commercial, Laborchemie Apolda	500°C, 1 h, N_2
ZrO_2/comm2	–	commercial, Laborchemie Apolda	500°C, 1 h, N_2
ZrO_2/A/untreated	A	untreated	500°C, 1 h, N_2
ZrO_2/B/untreated	B	untreated	500°C, 1 h, N_2
ZrO_2/B/untreated/air	B	untreated	500°C, 1 h, air
ZrO_2/aerogel	C		500°C, 1 h, N_2, 80–500°C, 5 h, air
ZrO_2/7%La_2O_3		coprecipitation in a $ZrO(NO_3)_2/LaCl_3$ solution with NH_3 (pH = 8)	500°C, 1 h, N_2
ZrO_2/amm.sulfite	A	obtained by kneading 85wt% of the metal oxide hydrate and 15wt% of the appropriate ammonium salt	5K/min up to 500°C, 3 h 500°C isotherm
ZrO_2/amm.sulfate	A		
$ZrO_2/SOCl_2$/gas./150	A	$SOCl_2/N_2$ gas flow, 150°C, 1 h	150°C, 30 min, N_2
$ZrO_2/SOCl_2$/gas./500	A	$SOCl_2/N_2$ gas flow, 150°C, 1 h	5 K/min up to 500°C, 3 h 500°C isotherm
$ZrO_2/SOCl_2$/refl./200	A	$SOCl_2$, reflux, 1 h	200°C, 30 min, N_2
$ZrO_2/SOCl_2$/refl./500	A	$SOCl_2$, reflux, 1 h	5K/min up to 500°C, 3 h 500°C isotherm

verted into relative values (arbitrary units). Since for all measurements exactly the same weights were used, the relative values represent mass related quantities.

The acidities of the catalysts are given in table 1 for two stages of the solid samples. First, solids obtained from the calcination process were analyzed before using in hydrolytic reaction (cf. table 1). Catalysts which were already used for the hydrolysis reactions (cf. table 2) were left in the reactor after shutting off the CFC and H_2O gas flow for 15 min in a dried N_2 stream ($1.5\ \ell/h$) at 500°C and then directly used for acidity determination as described above.

3. Results

3.1. *Bulk properties*

Table 2 presents relevant bulk properties of the zirconium oxide samples whose preparation and calcination was already described in the experimental section (table 1). Depending on the specific treatment of the sample, various crystal modifications of zirconia were obtained. The monoclinic structure is usually favoured in the temperature region where the experiments were carried out. However, the cubic structure was stabilized in many cases, e.g. by kneading amorphous $ZrO_2 \cdot xH_2O$ with ammonium sulfate and subsequent calcination (see table 1). This is in agreement with the literature. Narayanan et al. [10] found that an addition of the sulfate ion into $Zr(OH)_4$ helps to retain the cubic phase up to 550°C, whereas the untreated sample already exhibits the monoclinic structure at this temperature. As can be seen from table 2, a cubic zirconia can be prepared by several methods. Tetragonal zirconia was obtained from the calcined aerogel, but it must be mentioned here, that clear distinguishing between these two phases was difficult due to the similarity of the powder patterns and the peak broadening (low crystallinity).

Table 2 also indicates that all samples which were synthesized from $ZrOCl_2$ still contain traces of chloride. Treatment with $SOCl_2$ leads to an increase of the Cl content, but most of Cl is lost after using the samples as catalysts for hydrolysis of CFC-12. A similar behavior was observed with the sulfur content in the samples $ZrO_2/SOCl_2$/gas./500 and $ZrO_2/SOCl_2$/refl./500. In contrast to these samples, the ammonium sulfate and sulfite treated samples retained their comparatively high sulfur content. Obviously, the sulfate and sulfite complexes formed on the surface of zirconia were stable against the CFC-12/water vapour attack even at 500°C. The nature of these sulfate and sulfite complexes is discussed in ref. [8] and the references cited therein.

Small amounts of fluoride (between 0.4 and 0.3 wt%) were captured by the catalysts (120 min CFC-12 and water vapour at 500°C). In the absence of water, the degree of the catalyst fluorination increases considerably, as can be seen from tables 2 and 4. Obviously, water prevents the complete fluorination of the solid by permanent hydrolysis of Zr–F bonds.

3.2. *Surface properties and catalytic screening*

Table 3 compares surface properties of modified zirconium oxide catalysts before and after exposure to CFC-12/ water vapour (120 min, 500°C). The specific

Table 2
Catalyst characterization before and after CFC hydrolysis at 500°C (bulk properties)

Sample notation	XRD detected phases		Element content (wt%)				
	before	after catalysis	Cl		F after	S	
			before	after		before	after
ZrO_2/comm1	monocl. ZrO_2	monocl. ZrO_2	–	0.82	0.44	–	–
ZrO_2/comm2	monocl. ZrO_2	monocl. ZrO_2	–	0.48	0.63	–	–
ZrO_2/A/untreated	monocl. ZrO_2	monocl. ZrO_2, traces ZrO_xF_y	0.66	0.82	1.98	–	–
ZrO_2/B/untreated	cubic ZrO_2	monocl. ZrO_2	–	0.18	1.04	–	–
ZrO_2/B/untreated/air	cubic ZrO_2	monocl. ZrO_2	–	0.28	1.72	–	–
ZrO_2/aerogel	tetragonal ZrO_2	monocl. ZrO_2	–	0.54	1.73	–	–
ZrO_2/7%La_2O_3	cubic ZrO_2	monocl. ZrO_2, traces ZrO_xF_y	–	0.06	2.63	–	–
ZrO_2/amm.sulfite	cubic ZrO_2	monocl.ZrO_2, traces orthorh. $Zr_7O_9F_{10}$	0.42	0.38	1.56	2.12	0.3
ZrO_2/amm.sulfate	cubic ZrO_2	ZrO_xF_y, traces monocl. ZrO_2	0.40	0.43	2.51	4.4	4.1
$ZrO_2/SOCl_2$/gas./150	amorphous		8.53			1.98	
$ZrO_2/SOCl_2$/gas./500	cubic ZrO_2	monocl. ZrO_2	2.25	0.34	0.76	0.25	0.05
$ZrO_2/SOCl_2$/refl./200	amorphous		17.7			0.42	
$ZrO_2/SOCl_2$/refl./500	cubic ZrO_2	monocl.ZrO_2, orthorh. $Zr_7O_9F_{10}$	4.25	0.74	1.74	0.09	0.01

Table 3
Catalyst characterization before and after CFC hydrolysis at 500°C (surface properties) and CFC product composition

Sample notation	BET surface area (m^2/g)		Amount of acid sites (a.u.)				Gas product composition (mol%) (from 5 to 120 min time on stream)		
	before	after	Lewis		Brønsted		CFC-12	CFC-13	CO_2
			before	after	before	after			
ZrO_2/comm1	19	16.3	2	9	8	3	38–65	20–8	40–26
ZrO_2/comm2	20.3	14.5	8	8	5	5	46–83	10–6	43–15
ZrO_2/A/untreated	41	25.3	35	5	0	18	0	20–17	78–74
ZrO_2/B/untreated	153	23.8	23	7	14	35	0	7–10	91–88
ZrO_2/B/untreated/air	122	44.0	47	6	0	43	0	10–11	89–84
ZrO_2/aerogel		50.8		7		20	0	17	83
ZrO_2/7%La_2O_3	106	23.8	27	3	0	33	0	8–9	93–90
ZrO_2/amm.sulfite	157	27.8	41	1	25	29	0	2–5	95–91
ZrO_2/amm.sulfate	139	16.6	16	0	57	24	0	1–5	98–92
ZrO_2/$SOCl_2$/gas./150	367		13		33				
ZrO_2/$SOCl_2$/gas./500	73.5	29.1	6	2	12	18	0	2–17	96–81
ZrO_2/$SOCl_2$/refl./200			6		57				
ZrO_2/$SOCl_2$/refl./500	93.3	56.7	0	9	12	18	0	15	83–77

surface areas drop to lower values after catalysis possibly due to the formation of crystallized oxyfluorides in the surface region and due to the blockage of inner pores.

Moreover, the amount of acid sites changes. Lewis acid sites are reduced during the catalytic process, whereas the number of Brønsted sites is enlarged (except for ZrO_2/amm.sulfate). Apparently, a certain amount of Lewis acid sites is transferred into Brønsted sites by the addition of water during the catalysis. ZrO_2/amm. sulfate ("solid superacid") looses some of its Brønsted sites, possibly the most reactive sites. The two commercial samples show comparatively low acidities and a different behaviour. The low acidity corresponds to the low catalytic activity (large amounts of unconverted CFC-12, see table 3). All other samples show almost 100% conversion of CFC-12, but they differ in the amount of CFC-13 produced. CFC-13 may originate from disproportionation with subsequent hydrolysis of the higher chlorinated species CFC-11 and tetrachloromethane or can be formed via fluorination of CFC-12 by HF released during the hydrolysis.

A general correlation between the CFC-13 content and the amount of, e.g., Lewis acid sites is not observed. Nevertheless, those samples which exhibit the smallest CFC-13 concentrations possess only negligible amounts of Lewis sites, e.g. ZrO_2/amm.sulfate or ZrO_2/amm. sulfite.

3.3. Effect of water

The influence of water on the catalytic activity and stability of the catalyst (ZrO_2/amm.sulfate) is illustrated in figure 1. After 120 min on stream, the water vapour was shut off resulting in significant changes of the gas composition. The CFC-13 concentration immediately dropped to a small value and small amounts of CFC-11 and CFC-10 appeared. Since the decrease in CFC-13 concentration was obtained for all samples we conclude that the main portion of CFC-13 originated from fluorination of CFC-12 instead of disproportionation. After shut-off of water the hydrolysis and therefore the HF release was suppressed. Consequently, CFC-13 should also decrease if not formed via disproportionation.

The CO_2 curve shows a significant increase after 120 min due to the complete conversion of CFC-12 and due to the absence of CFC-13 during the period from 120 min to approximately 150 min. Due to the lack of

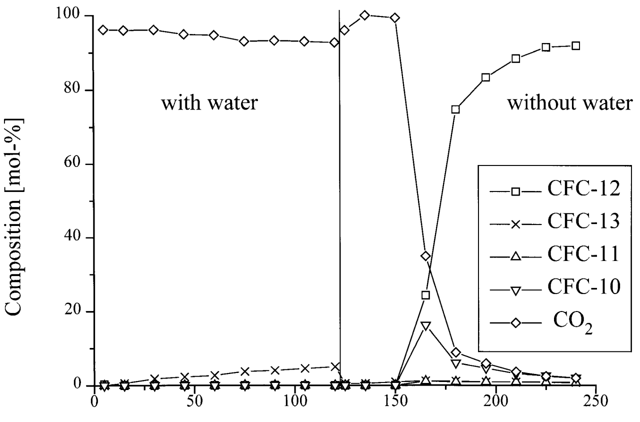

Figure 1. Gas product composition (C-containing species) with time on stream for the catalyzed hydrolysis of CFC-12 on ZrO_2/amm.sulfate at 500°C, before and after shut-off of the water vapor.

Table 4
Characterization of catalysts after shut-off of water vapor (only CFC-12, 500°C, 120 min)

Sample notation	XRD detected phases	Element content (wt%)			BET area (m^2/g)	Amount of sites (a.u.)	
		Cl	F	S		Lewis	Brønsted
ZrO_2/comm1	monocl.ZrO_2, tetr.$ZrF_{3.3}O_{0.33}$, orthorh. $Zr_7O_9F_{10}$	0.44	6.8		5.4	4	4
ZrO_2/A/untreated	tetragonal ZrF_4	3.16	22.9		0.3	5	4
ZrO_2/amm.sulfate	tetragonal ZrF_4, orthorh. $Zr_7O_9F_{10}$	2.46	26.4	0.5	3.1	4	5

water in the gas phase, both adsorbed water and surface OH groups are consumed and not generated. Interestingly, the activity remains high resulting in high conversion degrees of CFC-12 even with decreasing Brønsted acid sites. After about 30 min, the CFC-12 conversion decreases. At the same time there is a considerable maximum of CFC-10 (CCl_4). It can be assumed that adsorbed hydrogen chloride and/or Zr–Cl species act as chlorination agents in absence of water. This function was suppressed during the catalyzed hydrolysis since HF was present in the system. In this case, HF reacts directly with the solid to form oxyfluorides and fluorides. Since water is not present at this stage, the degree of catalyst fluorination is much higher than in the hydrolysis period. Therefore, considerably higher fluoride contents were obtained for the samples after shut-off of water (table 4). This is accompanied by a decrease in specific surface area and number of acid sites. The catalyst has been deactivated as a result of the fluorination.

3.4. Effect of temperature

Figure 2 presents the gas product curves versus time on stream for the ZrO_2/amm.sulfate-catalyzed hydrolysis of CFC-12 at 300 and 500°C, respectively. Fresh samples were used in both cases. It is remarkable that the highly Brønsted acid sample ZrO_2/amm.sulfate is able to decompose CFC-12 almost completely at 300°C already. Unfortunately, after approximately 15 min the conversion of CFC-12 sharply decreases to 10%. Table 5 confirms that a certain amount of Brønsted and Lewis sites will be consumed and not regenerated at this low temperature. Although there is still a considerable amount of Brønsted sites, the CFC-12 conversion does not exceed 10% at the end of operation. This can be explained by the relatively low temperature.

Instead of the regeneration of OH groups, the fluorination of the catalyst occurs as confirmed by the lack of HF in the gas. The fluorination of the solid is irreversible, a hydrolysis of Zr–F bonds does not take place at this temperature. The F content of the solid sample is much higher than those of the 500°C operation (table 5).

At 500°C, the concentration of acid sites is diminished but it has approached a stable amount which is obviously sufficient for an almost complete CFC-12 conversion at this high temperature. The excess of HCl in comparison with HF is not as large as in the case of 300°C operation. Obviously, a permanent regeneration of the acid sites takes place under these conditions.

Before catalysis, the catalyst ZrO_2/amm.sulfate possessed mainly Brønsted acid sites and almost no Lewis acidity. This situation made it possible to decompose the

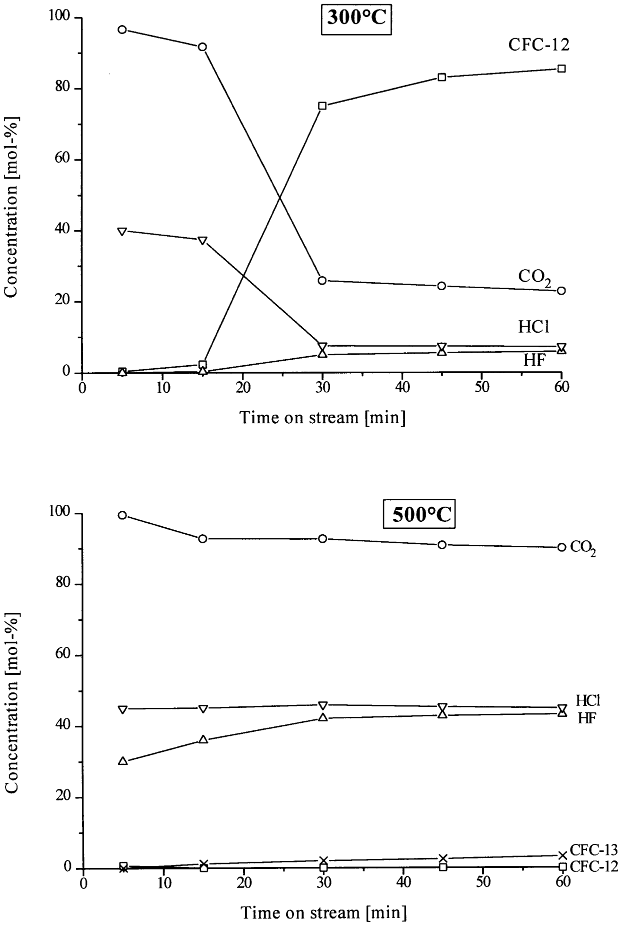

Figure 2. Gas product concentrations with time on stream for the catalyzed hydrolysis of CFC-12 on ZrO_2/amm.sulfate at 300 and 500°C, respectively (total of C-containing species = 100%, total of theoretically expected acid gases = 100%).

Table 5
Catalyst characterization after low temperature CFC hydrolysis at 300°C

Sample notation	XRD detected phases	Element content (wt%)		Amount of sites (a.u.)			
		Cl	F	Lewis		Brønsted	
				before	after	before	after
ZrO_2/A/untreated	tetragonal and monoclinic ZrO_2	0.2	4.0	47	52	0	2
ZrO_2/amm.sulfate	tetragonal and monoclinic ZrO_2	0.4	7.4	16	5	57	42

halocarbon at 300°C during the initial period of operation. In contrast to this, the sample ZrO_2/B/untreated/air possessed only Lewis acid sites before catalysis (table 3). It is therefore not surprising that the reaction does not take place at this sample under comparable conditions (300°C, figure 3). The number of acid sites does not change significantly compared with the calcined sample (tables 3 and 5). At 500°C, a permanent hydrolysis of the majority of Zr–F species takes place resulting in the formation of new Brønsted acid sites (table 3) and leading to a large CFC-12 conversion (figure 3).

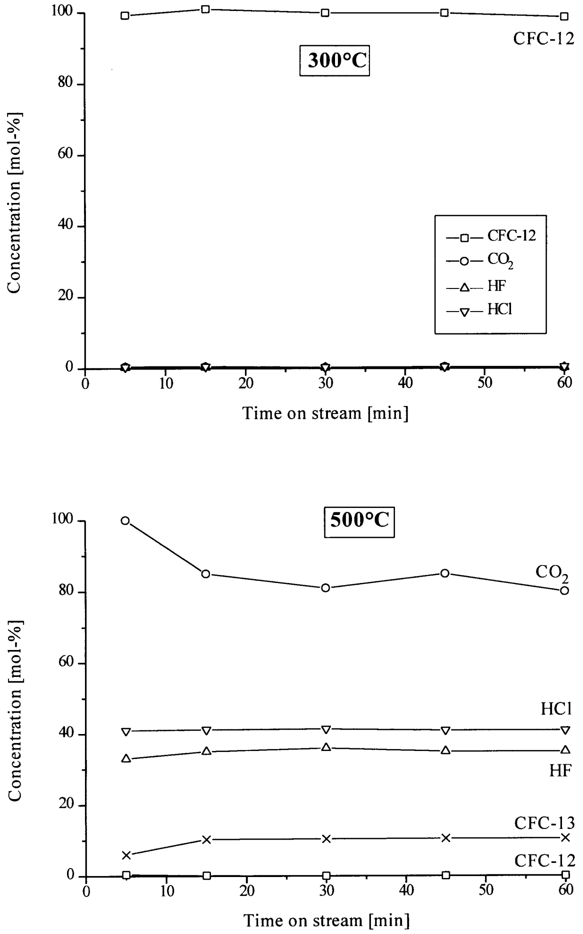

Figure 3. Gas product concentrations with time on stream for the catalyzed hydrolysis of CFC-12 on ZrO_2/B/untreated/air at 300 and 500°C, respectively (total of C-containing species = 100%, total of theoretically expected acid gases = 100%).

3.5. Catalyst activity and conversion

Some of our catalysts were tested under similar reaction conditions as reported by Imamura et al. [4]. The initial partial pressure of CFC-12 and the residence time were significantly lower than in our apparatus:

Imamura [4]: CFC-12 0.6%, water 1%, oxygen 20.6%, helium 77.8%;
$T = 550$°C; residence time 0.6 s (SV $= 6000\ h^{-1}$);
this work: CFC-12 10.5%, water 25.2% in nitrogen;
$T = 500$°C; residence time 3 s.

The samples ZrO_2/B/untreated/air and ZrO_2/amm.sulfate were selected for the comparison of the activity and conversion. 100% conversion were achieved similar to boron phosphate which was found to be a very good and stable catalyst [4]. Between 2 and 17% CFC-13 in the reaction gas were obtained during our tests. Unfortunately, the extent of the CFC-13 formation on BPO_4 was not reported in the literature.

Considering the absence of oxidizable reactants in the system, the reasons for the application of O_2 for the CFC-12 decomposition as has been used by many authors are not clear. In CFC-12, carbon is already in its highest oxidation state. Oxidizable coke deposits were also not observed under the experimental conditions.

Summarizing, the samples ZrO_2/B/untreated/air and ZrO_2/amm.sulfate were found to be highly active and competitive catalysts.

4. Conclusions

A heterogeneous catalyst for the hydrolytic decomposition of CFC-12 should have the following properties:

– Brønsted acid sites are required or should be formed in situ.

– A permanent hydrolysis of metal–F bonds for a regeneration of the Brønsted acid sites under the reaction conditions should be possible.

– Lewis acid sites only serve when they can be transformed into Brønsted acid sites, otherwise they are responsible for undesired side reactions (e.g. disproportionations, fluorinations etc.).

Considering the results, it is evident that CFC-13 is formed by heterogeneously catalyzed fluorination of CFC-12 with HF. A mechanism based on the disproportionation of CFC-12 into CFC-11 and CFC-13 with subsequent hydrolysis of the less stable CFC-11 can be excluded.

The mechanism of the catalytic step is not entirely clear. There are two possible routes. Firstly, the Brønsted acid OH groups simply polarize the halocarbon to enable a subsequent attack by the water molecule. The second and more likely mechanism is based on a heterogeneous reaction between the halocarbon and the OH group forming a metal–fluorine bond. The latter is hydrolyzed in a second step to regenerate the OH group. The results of the present work support this.

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