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Studies on the catalytic dechlorination and abatement of chlorided VOC: the cases of 2-chloropropane, 1,2-dichloropropane and trichloroethylene

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Abstract

The conversion of monochloropropanes and dichloropropanes over acid catalysts has been investigated in the presence of oxygen. In the temperature range of 450–550 K, dehydrochlorination of monochloropropanes to propene and HCl occurs selectively over silica–alumina, while significant formation of chlorinated by-products is observed over ZSM5 zeolite catalyst even at higher temperatures. Dichloropropanes conversion over silica–alumina catalyst gives rise mainly to chloropropenes in the temperature range 500–700 K. CO_x are predominant products only at the highest reaction temperatures (just above 700 K). Water vapor in the feed only slightly affects conversions and selectivities. Deactivation processes occur upon dichloropropane conversion, mainly due to coke deposition.

The conversion of highly chlorinated compounds, such as trichloroethylene (TCE) has been tested over silica–alumina and over HY zeolite in the presence of water vapor in the so-called “steam reforming” conditions (HVOC:water = 1:2). With diluted feed (1200 ppm) on HY, reaction occurs above 800 K and formation of chlorinated by-products is minimized, CO_x being the main reaction products. At higher HVOC concentrations conversion is obtained at even lower temperature (600 K), but no more negligible by-products formation has been detected. In our conditions zeolite catalyst is more effective in TCE total conversion than silica–alumina. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Dechlorination; Chloropropanes; Acid catalysts; Trichloroethylene; Silica-alumina; HY zeolite; HVOC abatement

1. Introduction

The abatement of chlorinated volatile organic compounds is needed in the treatment of several gaseous industrial wastes. Deep oxidation of chlorinated hydrocarbons has been studied over noble metal-based catalysts and over chromia–alumina catalysts [1]: major drawbacks of this technology are the catalyst deactivation by chlorine species, the expensiveness of the catalysts and their own toxicity.

Gonzalez-Velasco and co-workers [2] pointed out that also acidic catalysts and zeolites (H-type) have promising activity in the destructive oxidation of chlorinated volatile organic compounds, such as dichloroethane and trichloroethylene (TCE) [3] both in dry and wet conditions.

Alternatively elimination of chlorine atoms from HVOC compounds in gas phase can be performed catalytically in the hydrodechlorination process over noble metal-based catalysts, in the presence of

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hydrogen or hydrogen supplying compounds [4,5]. Major drawbacks in this case are the need of hydrogen or hydrocarbons storage, the use of high reaction pressures and the use of noble metals.

In the case of a weakly chlorinated hydrocarbon also dehydrochlorination reaction can be considered in order to obtain low-chlorine containing products, which could allow the HCl recovery prior to incineration [6,7].

Catalytic steam reforming of chlorocarbons over Ni-supported catalysts has also been proposed as an interesting alternative to the conventional processes in particular for heavily chlorided compounds. The presence of stoichiometric water appears to hinder coke deposition and catalyst deactivation, reducing at the same time chlorinated by-products formation [8].

In the present work we summarize our results on the conversion of chlorinated hydrocarbons over different acidic catalysts, in the presence or absence of water vapor. The aim is to develop new noble metal free, chromium free and nickel free catalysts which allow the destruction of chlorided compounds at ambient pressure, without need of hydrogen and allowing the recovery of chlorine as HCl.

2. Experimental

The acidic catalysts investigated are described in Table 1. Catalytic tests have been carried out in a continuous fixed bed tubular flow reactor. 0.1–0.5 g of catalysts was loaded in the form of fine powder (60–70 mesh, except in the case of HY zeolite, 30–40 mesh). Liquid chloropropanes (1-chloropropane or 1-CP, 2-chloropropane or 2-CP) and dichloropropanes (1,2-dichloropropane or 1,2-DCP and 1,3-dichloropropane or 1,3-DCP) were from Aldrich. TCE has been fed as gaseous mixture with helium (from SIAD) and as liquid (from Aldrich). The feed composition considered in the experimental runs was fixed at 1200 ppm of chlorinated compounds and in some cases was raised to 10,000 ppm of HVOC in helium. The presence of excess oxygen allow us to simulate a possible waste gas (from or previous incineration). Most of the experiments were consequently carried out with a GHSV ranging from 37,000 to 12,400 h^{-1}. The reactants and the reaction products were analyzed on line using a gas chromatograph (HP 5890) equipped with a HP PLOT Q column connected to a TCD and an FID detector. A methanizer allowed the analysis of CO and CO_2. GC–MS analysis of the products has been performed using a HP GCD G1800B instrument with an HP-VOC column. A refrigerated bubbler containing toluene has been placed at the end of the catalytic line, in order to trap heavier reaction products from TCE conversion.

Table 1
Catalysts investigated

Catalyst	Origin	Composition	Surface (m^2/g)
SiO_2–Al_2O_3	STREM	87% SiO_2–13% Al_2O_3	330
ZSM5	Zeolyst	Si:Al = 30:1	>400
HY	Grace	Bulk SiO_2/Al_2O_3 mole ratio = 10	800–850

To analyze HCl and Cl_2, the effluents were contacted with NaOH water solution. Chloride and hypochlorite anions have been analyzed and quantified by means of ionic chromatography. Actually, hypochlorite anions were never detected upon dehydrochlorination. HCl only is produced in this case and always nearly fulfilled the chlorine balance, if organic chlorided compounds analyzed by GC and GC–MS are taken into account. Upon TCE conversion chlorine is found when no water is fed. So, in this work only conversion and selectivities based on carbon-containing compounds are considered. Infrared spectra have been recorded by a Nicolet Magna 750 instrument connected to a conventional gas manipulation apparatus, using pure powder self-supporting disks (around 30 mg).

3. Results and discussion

As previously reported [7] complete conversion of 1-CP and 2-CP over alumina and silica–alumina has been reached at quite low temperatures, around 480 K on alumina and at 450 K on silica–alumina catalysts. Moreover, over these catalysts selectivity to propene and HCl is almost total, chloropropenes in traces being the main by-reaction chlorided products. Over alumina-based catalysts, we observed an effect due to the chlorine atom position: 2-CP reacts faster than the primary isomer, thus indicating the possible formation of a carbenium ion (secondary vs.

primary) as intermediate or transition state. FT-IR studies pointed out the formation of alkoxy species at the catalyst surface after heating in the presence of chloroalkane. Desorption of alkene from alkoxide is also observed from infrared and is supposed to be the rate determining step of the reaction. HCl desorption is also observed nearly simultaneously.

2-CP conversion over ZSM5 starts above 400 K, but selectivity to propene is low, due to by-products formation in large amount. After the catalytic run the catalyst is completely black and IR analysis shows bands characteristic of coke at the surface (CC stretching mode) [7].

Silica–alumina seems to perform the best results in 2-CP dechlorination, both from the point of view of low activity temperature and high selectivity to propene, thus the catalyst has been submitted to further investigations. In the case of dichloropropanes our data [9] indicate that in the temperature range 400–700 K the dehydrochlorination catalytic activity occurs in two successive steps. The first one gives rise to three chloropropene isomers ((*E*)-1-CP =, (*Z*)-1-CP =, and 3-CP = chloropropenes) starting from 1,2-DCP, while at higher temperatures (>700 K) it is possible to identify allene-like species and/or propyne (P), thus indicating a further dehydrochlorination step. As in the case of 1-CP and 2-CP the faster reaction of 1,2-DCP in comparison with the reactivity of 1,3-DCP can be explained by the formation of a carbenium-like species, due to the secondary C–Cl bond breaking instead of primary C–Cl bond breaking (Fig. 1). In agreement with these data monochlorinated compounds are dehydrochlorinated easier than dichlorinated propanes. Water vapor fed in 1:2 (HVOC:water) ratio has no significant effect on 1,2-DCP conversion (Fig. 2), while it slightly changes products distributions. At the highest reaction temperatures the selectivity to (*E*)-1-CP= isomer is apparently enhanced (i.e. 30% selectivity vs. 10% in the case of dry conditions), possibly due to a lower activation energy for the *syn*-elimination on chloropropene with respect to the *anti*-elimination. CO_2/CO ratio increases, maybe due to WGS reaction, but no higher selectivity to CO_x is observed. Both in the case of dry conditions and in wet conditions the catalyst surface is heavily coked after the catalytic run, even in the presence of oxygen.

FT-IR data indicate also in this case the formation of alkoxy species at the surface and also the formation of a carbonyl species (likely acrolein) in the gas phase [9]. This compounds could be precursor of CO_x (or coke).

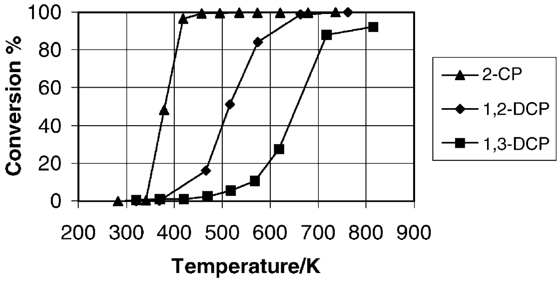

Fig. 1. 2-CP, 1,2-DCP and 1,3-DCP conversion over silica–alumina catalyst (0.1 g catalyst, 1200 ppm HVOC, dry conditions, excess oxygen, total flow: 350 ml/min).

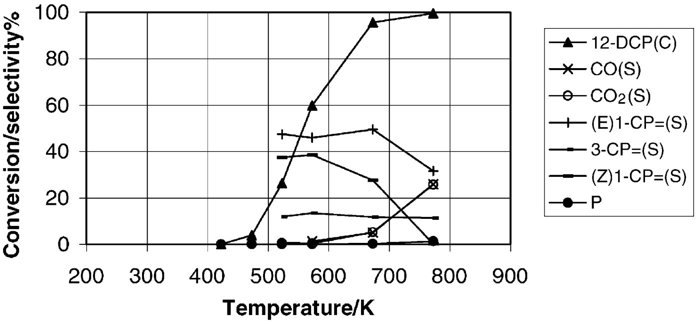

Fig. 2. 1,2-DCP conversion (C) in wet conditions over silica–alumina catalyst, and selectivity (S) to chloropropenes (1-CP= isomers and 3-CP =), propyne (P) and CO_x (same reaction conditions as in Fig. 1).

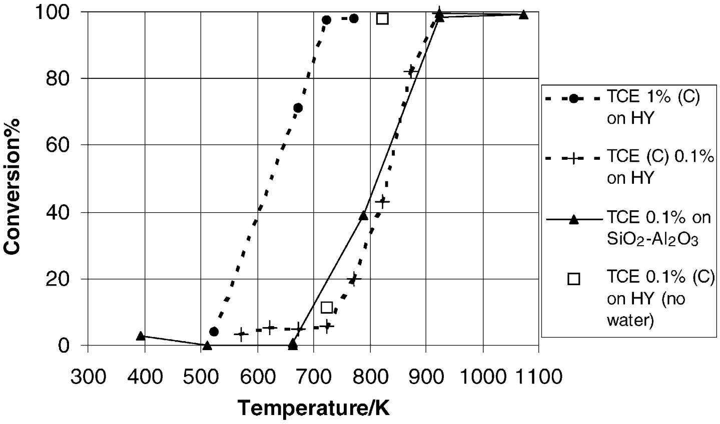

Fig. 3. TCE conversion over silica–alumina (GHSV = 37,200 h^{-1}) and over HY zeolite catalysts ($p_{TCE} = 0.001$ atm and $p_{TCE} = 0.01$ atm) in dry and humid conditions.

TCE conversion has been tested over the silica–alumina catalyst as an example of a highly chlorinated hydrocarbon which is refractory to dehydrochlorination (Fig. 3). High GHSV (37,200 h^{-1}) due to low catalyst content in the reactor does not allow high conversion (10% conversion at 800 K) and in these conditions water vapor in the feed definitely increases conversion, up to 40% (Fig. 3) at temperature slightly higher than 800 K. Selectivity to CO_x approaches 100% but the CO/CO_2 ratio is strongly in favor of CO (around 4 at the lower temperatures), while at increasing temperature CO_2 formation increases but is still half of the CO amount formed, even in excess oxygen. By-products are present in traces at temperatures above 723 K (tetrachloroethylene) and above 813 K (dichloroethylene) as identified by GC–MS analysis. As reported in the literature, in the case of zeolites, alumina-based and perovskite type catalysts, their formation can be hindered by water vapor in the feed [3,10,11]. On silica–alumina at the lowest GHSV (12,400 h^{-1}) complete TCE conversion is reached at 900 K and the ratio CO/CO_2 is near 4. No relevant deactivation phenomena are observed after 10 h on stream. The spent catalyst is still white indicating that in the reaction conditions (i.e. in the presence of oxygen) no coke deposition occurs. CO_x are the main products with selectivity near to 100%, but still the CO/CO_2 ratio is quite high. Activation energy around 46 kJ/mol indicated the chemical regime, while at increasing catalytic bed volume, however, corresponds decreasing activation energy, down to 10 kJ/mol, thus diffusion phenomena become relevant. Deactivation does not occur, at least in the 30 h runs tested.

The conversion of TCE (1000 ppm) on HY in the presence of excess water starts to be detectable at 600 K and is complete only at 920 K. Lowering the vapor fed down to 2000 ppm increases the conversion without changing the selectivity profile. On the other side, TCE conversion in the catalytic run without water reaches high values at comparatively low temperatures (Fig. 3), but significant Cl_2 formation (to be preferably avoided) is observed in these conditions, as also reported in the literature [3,11].

In this HVOC concentration range the presence of oxygen, fed in great excess to simulate conditions of waste gases, does not influence the conversion: without oxygen the conversion is completely consistent with the results obtained in oxidizing conditions. The ratio CO/CO_2 is actually exceeding the values obtained in other catalytic runs (around 15 vs. 4–5). During this catalytic run the catalyst starts to show partial coke effect, becoming gray, but the activity can be recovered by regeneration in oxygen/helium mixture at high temperature.

At higher HVOC concentrations (TCE:10,000 ppm/water:20,000 ppm) total conversion is reached at significantly lower temperatures. The formation of reaction by-products (tetrachloroethylene) is significant, starting to be detectable at 673 K and peaks at 723 K, then decreases to traces amount.

4. Conclusions

The studied acidic catalysts are active in the dehydrochlorination of mono- and dichloropropanes: silica–alumina performs the best catalytic results both from the point of view of conversion temperatures and selectivity to alkenes and HCl.

In the 500–700 K temperature range dichloropropanes are actually converted to chloropropenes which are still present at high temperatures. A second dehydrochlorination step then takes place and final reaction products are CO_x and HCl. Deactivation occurs in several tenths of hours of activity, even in the presence of oxygen.

TCE conversion over the same catalyst (reactor loaded with 1.5 g catalyst, wet conditions) approaches 100% around 900 K, being CO_x and HCl the predominant reaction products. We do not have evidence of coke deposition at the catalyst surface during 30 h activity. A first series of catalytic runs pointed out an even higher activity of the HY catalyst, which can be further evaluated.

The main conclusions of this work is that catalytic destruction of chlorinated compounds without noble metal and without the use of hydrogen is possible with acid catalysts such as silica–alumina and protonic zeolites. With weakly chlorided aliphatic hydrocarbons dehydrochlorination occurs at low temperature and water and O_2 have no definite positive effects. For heavily chlorided compounds (TCE) water is needed to perform steam reforming. However, reaction temperatures lower than 700 K can be used only with concentrated feeds and in this case selectivity to CO_x is not so high. Efforts are still in progress to develop catalysts active in a temperature range where the formation of dioxine can be excluded (i.e. below 700 K).

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