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Catalytic oxidation of aliphatic chlorinated volatile organic compounds over Pt/H-BETA zeolite catalyst under dry and humid conditions

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Abstract

The present study investigated the applicability of noble metal/H-zeolite catalysts for the oxidative decomposition of chlorinated VOCs, and specifically compared the activity and selectivity of Pt/H-BETA with that of an H-BETA for the combustion of dichloromethane and trichloroethylene (1000 ppm in dry and humid air) between 200 and 550 °C at a space velocity of 15,000 h^{-1}. A preliminary study identified the superior catalytic properties of H-BETA as an eventual support for a supported noble metal catalyst compared to other conventional supports such as Al_2O_3, ZrO_2 and SiO_2. The primary catalytic property for predicting activity in oxidative decomposition reactions was observed to be the total acidity of the support.

Platinum played a major role in influencing the catalytic properties of H-BETA for complete oxidation of the chlorinated volatile organic compounds. Thus, the activity of the resultant Pt/H-BETA catalyst was noticeably enhanced, and the production of CO_2 and Cl_2, the products of CO oxidation and the Deacon reaction, respectively, was largely favoured. The addition of 15,000 ppm of water was found to improve the performance of the Pt/H-BETA catalyst, since the destruction temperatures were significantly lowered and the levels of molecular chlorine and chlorinated by-products were greatly reduced.

Keywords: Catalytic combustion; Chlorinated VOCs; Platinum; Zeolite BETA; Water

1. Introduction

Increased production and application of chlorinated VOCs are causing increasing concern with respect to the proper disposal and destruction of these hazardous waste materials. Chlorocarbons are widely used in industry as solvents, have a high chemical and thermal stability and tend to accumulate in the environment [1]. Consequently, the development of adequate abatement technologies for the reduction of these harmful gaseous emissions is of paramount importance. Several clean-up technologies, such as thermal oxidation and catalytic oxidation, are widely known and used today for treating gas phase emissions from industrial plants. In conventional incineration methods, temperatures exceeding 700 °C are required to obtain complete decomposition [2]. In the case of low concentration levels of contaminant (<1000 ppm) in the gas phase, the process becomes exceedingly inefficient, as the entire sample must be heated to the combustion temperature. Indeed, the cost of the fuel alone can account for about 40% of the total operating cost [3]. Furthermore, the combustion of chlorinated hydrocarbons presents additional complications. For instance, chlorine-containing materials are known to inhibit flame propagation and have low combustion heats. As a result, the development of low-temperature processes for chlorinated waste disposal can offer significant improvements over traditional thermal oxidation.

Probably the most appropriate (and economical) method for treating dilute oxygen-containing waste gases is catalytic combustion [4]. Since large volumes have to be treated, the catalytic process has to be performed at relatively high space

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velocity ($>10{,}000\ \mathrm{h}^{-1}$), and this requires a very active catalyst. An additional difficulty in catalytic VOC removal comes from the fact that the stream may contain organic compounds of a very different chemical nature. Finally, the catalyst must maintain its activity in the presence of species such as water vapour.

A catalytic combustion process, if properly designed, must lead to the complete destruction of all kinds of chlorinated VOCs, including the harmful by-products which can be produced by an incomplete destruction of the starting chlorocarbon. The catalytic combustion is also interesting on account of the potential selectivity to harmless final products. The desired selectivity of an ideal catalytic combustion of chlorinated waste would be the formation of water, carbon dioxide and hydrogen chloride. HCl is the preferred chlorinated product since it can be easily removed by washing the off-gases and does not lead to the formation of more harmful polychlorinated compounds. Taking these points into consideration, research in the heterogeneous catalytic oxidation of low concentrations of chlorinated hydrocarbons with air must focus on identifying highly active catalysts and obtaining benign reaction products at moderate temperatures. As a result, reaction conditions resulting in complete oxidation to H_2O, CO_2, and HCl must be chosen.

Noble metal-based catalysts have been widely for the oxidation of chlorinated VOCs because of their noticeable intrinsic activity and selectivity to CO_x [5–7]. Generally, palladium catalysts are slightly more active, while platinum catalysts are more selective to CO_2 [8]. Typically, the most common supports for this type of catalysts are alumina, zirconia and silica. It is well known that the characteristics of the support can play a significant role in determining catalytic performance [9–13]. Particularly notable catalytic effects have been assigned to the acidic properties of the support due to the implication of acid sites in several steps in combustion processes [14]. Recent studies on the applicability of H-type zeolites as potential catalysts for chlorocarbon destruction evidenced that acid sites, mainly Brønsted-type sites, acted as efficient chemisorption sites for chlorinated molecules [15,16]. As a result, combustion temperatures were markedly decreased in comparison with the thermal decomposition. Moreover, surface acidity significantly inhibited the selectivity to molecular chlorine in favour of the desired chlorinated deep combustion product, HCl [17]. Therefore, the combination acidic and oxidising characteristics makes platinum-doped zeolites potentially interesting as combustion catalysts for chlorinated VOC abatement.

The operating conditions selected for this study, namely the nature of the chlorinated VOCs, the concentration (1000 ppm), the contact time (0.24 s) and the presence of water vapour (15,000 ppm), are representative of conditions of VOC removal in industrial effluent streams. The classes of compounds investigated in this study include chlorinated methanes and chlorinated ethylenes. These were chosen because chlorinated methanes and ethylenes have been ranked, respectively, as intermediate and low on their ease of destruction [18]. The specific compounds of dichloromethane (DCM) and trichloroethylene (TCE) were selected as typical compounds within these groups, and are also common chlorinated VOC pollutants. Hence, these two compounds may actually provide some representative information on the catalysts' ability to oxidise other chlorinated VOCs.

The objective of this study is to examine the applicability of Pt/H-BETA zeolite catalysts in the detoxification by combustion of waste gases containing low concentrations (1000 ppm) of dichloromethane and trichloroethylene. This study takes into account different aspects of chlorinated VOC removal, namely not only the destruction efficiency of chlorocarbons of a different chemical nature but also the product selectivity or the effect on catalytic performance of the presence of an excess of water (15,000 ppm) in the feed stream.

2. Experimental

2.1. Catalyst preparation

Zeolite NH_4-BETA (CP814E) with a SiO_2/Al_2O_3 molar ratio of 25 was supplied by the Zeolyst Corporation. The H-BETA form was obtained by calcining the ammonium form in air at 550 °C for 3 h. Platinum was introduced into the support using a tetraammineplatinum (II) nitrate salt (Aldrich). The required amount of $Pt(NH_3)_4(NO_3)_2$ salt precursor was added to a suspension of 5 g of H-BETA zeolite in 250 cm^3 of deionised water. After stirring for 24 h at room temperature, the slurry was filtered and thoroughly washed with deionised water to remove any soluble salts. Quantitative uptake of the metals occurred, as verified with atomic absorption spectroscopy on the filtrates. The sample was then dried overnight (12 h) at 110 °C in a convective oven. 0.3–0.5 mm diameter catalyst pellets were prepared by compressing the zeolite powders into flakes in a Specac hydraulic press, followed by crushing and sieving. The platinum loading expressed in weight percent (wt.%) on a dry zeolite weight basis was 0.7 wt.%.

The metal catalysts were activated by calcination at 550 °C, with a slow heating rate of 1 $°\mathrm{C\,min}^{-1}$ in air, and subsequent reduction at 300 °C with a 5%H_2/Ar stream. After activation, and before they were subjected to catalyst activity experiments, the catalyst pellets were characterised using several analytical techniques.

2.2. Zeolite catalyst characterisation

The metal content in the catalysts was measured by inductively coupled plasma–atomic emission spectroscopy (ICP–AES) in ARL Fisons 3410 + ICP equipment. The textural properties of the zeolite catalysts were measured with a Micromeritics ASAP 2010 analyser. The measure-

Table 1
Physicochemical properties of the supports and the metal zeolite catalyst

Zeolite catalyst	Surface area ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)	Crystallinity (%)	Total acidity (mmol $NH_3\ g^{-1}$)	Metal content (wt.%)	Dispersion (%)
SiO_2	323	1.20	n.a.	0.02	–	–
ZrO_2	50	0.25	n.a.	0.24	–	–
Al_2O_3	105	0.57	n.a.	0.35	–	–
H-BETA	580	0.68	100	0.63	–	–
Pt/H-BETA	571	0.67	96	0.61	0.7	31

n.a.: not analysed.

ments were performed on freshly prepared catalysts by recording adsorption and desorption isotherms of nitrogen at the temperature of liquid nitrogen. CO chemisorption measurements were performed at 25 °C using the same volumetric apparatus. The irreversible uptake of CO was measured using a dual isotherm technique, i.e., after determination of the first isotherm, the sample was evacuated at 25 °C for 30 min and a second isotherm was obtained. The difference between the two isotherms accounted for the amount of CO irreversibly held on the surface of the catalyst. A $CO_{irrev}/Pt = 1$ stoichiometry was taken as a reasonable estimate in determining Pt dispersion.

X-ray diffraction (XRD) studies were carried out on a Philips PW 1710 X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5406$ Å) as the incident X-ray source, and a Ni filter. Relative crystallinity was calculated on the basis of comparing the average intensities for most intense peaks for the parent versus treated zeolite catalyst. The starting H-zeolite was assumed to be 100% crystalline. Temperature-programmed desorption (TPD) of ammonia was performed on a Micromeritics AutoChem 2910 instrument. The desorption step was carried out from 100 to 550 °C at a constant heating rate of 10 °C min^{-1} in flowing helium. This temperature was maintained for 15 min until the adsorbate was completely desorbed. Details about the experimental procedure for each analytical technique are described in detail elsewhere [19].

2.3. Catalytic activity measurements

Catalytic oxidation reactions were carried out in a conventional fixed bed reactor at atmospheric pressure [20]. The flow rate through the reactor was set at 500 $cm^3\ min^{-1}$ and the gas hourly space velocity (GHSV) was maintained at 15,000 h^{-1}. Liquid chlorinated hydrocarbon (1000 ppm) and water (15,000 ppm) were injected into the dry air using syringe pumps. Details on the experimental procedure for reaction product analysis are given elsewhere [20].

3. Results and discussion

3.1. Characterisation results

The textural properties, crystallinity, metallic dispersion and acidic properties of the zeolite catalysts are listed in Table 1. Both the textural and structural properties of Pt/H-BETA were practically identical to those of the parent support. Only a slight decrease in the surface area and in the crystallinity of the noble metal zeolite catalyst was observed, thus providing evidence that the structure of the zeolite H-BETA was largely maintained after the incorporation of a relatively low amount of platinum. In accordance with textural and XRD analysis, the number of acid sites slightly decreased for the Pt/H-BETA catalyst compared to the original H-BETA. Similarly, the addition of a low amount of platinum to H-BETA did not significantly modify the acidic properties of this H-zeolite [19]. According to Borade and Clearfield, the nature of acid sites in H-BETA zeolite is Brønsted-type acidity [21]. Note that the total surface acidity of H-BETA is considerably higher than that of other supports (Table 1). On the other hand, a dispersion value of 31% was obtained from CO chemisorption measurements for the Pt/H-BETA catalyst. This result was consistent with that found by Garetto et al. [22].

3.2. Activity and selectivity results under dry conditions

Before studying the catalytic performance of H-BETA-based catalysts, a comparative analysis between the catalytic properties of several typical supports such as alumina, silica and zirconia, and those of pure H-BETA was carried out. The experiments were carried out at constant space velocity (15,000 h^{-1}) and chlorinated VOC feed concentration (1000 ppm in dry air). The textural properties and acidic characteristics of these supports are given in Table 1.

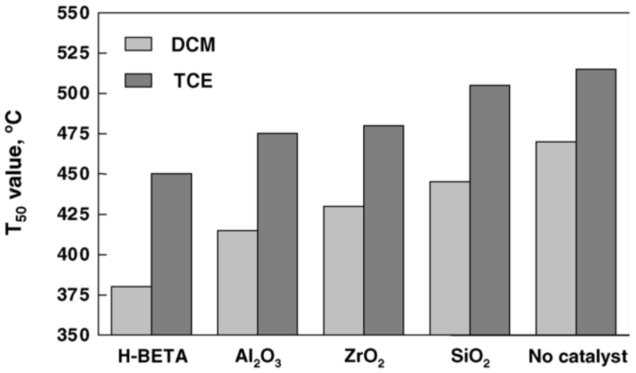

Fig. 1. T_{50} values obtained for the oxidative decomposition of DCM and TCE over various supports and in the absence of any catalyst (homogeneous reaction) under dry conditions.

Typically, catalytic activity was characterised by monitoring the rise in conversion as a function of temperature for a particular chlorinated VOC in given test conditions. A characteristic curve, referred to as the light-off or ignition curve, was obtained. T_{50} (temperature at which 50% conversion was reached) was used as an indicative of the relative reactivity of the catalysts. Fig. 1 shows the T_{50} values of the combustion of DCM and TCE over silica, zirconia, alumina and H-BETA supports, along with the T_{50} values corresponding to the homogeneous decompositions. The possibility of homogeneous gas phase reactions at the reaction temperature range studied was checked through an experiment placing crushed quartz into the reactor tube. It was found that all the catalysed reactions needed lower reaction temperatures than the homogenous reaction, irrespective of the catalyst or the chemical nature of the chlorinated feed. Taking into consideration the T_{50} values for the oxidative decomposition of both chlorohydrocarbons, decreasing activity of the various supports was detected in the following order: H-BETA > Al_2O_3 > ZrO_2 > SiO_2 > homogeneous reaction.

Contrary to the destruction of DCM, the supports investigated were notably less active in the conversion of TCE, and reaction only occurred at temperatures above 400–450 °C. The observed catalytic trends were fairly consistent with the order of the supports as function of their total acidity, thus pointing out the key role played by acid sites in the decomposition process. Similar results were obtained when comparing these supports with H-ZSM-5 zeolite, since this protonic zeolite also exhibited markedly lower temperatures for the decomposition of chlorinated VOCs in air [23]. Moreover, the potential activity of protonic zeolites for chlorocarbon destruction has previously been suggested in earlier existing papers [24,25]. Given the encouraging results obtained with blank H-BETA zeolite in the oxidative decomposition of chlorohydrocarbons, our attention was therefore focused on the study of a platinum-modified zeolite (Pt/H-BETA) catalyst which eventually would combine the catalytic properties of the zeolite support and of metallic sites, thus giving rise to an improved catalyst.

The light-off curves of the oxidation of both DCM and TCE over H-BETA-based catalysts are shown in Fig. 2. As shown in this figure, chlorinated VOC conversion with both catalysts increased progressively as the temperature was raised. The pure H-BETA proved significantly more active than H-Y (Si/Al = 2.4), and showed an activity comparable with that of H-ZSM-5 (Si/Al = 27) [18]. It was observed that the addition of a relatively low amount of platinum (0.7 wt.%) to H-BETA brought about a significant decrease in destruction temperatures for both chlorinated feeds investigated. Both the acid and the metallic sites of the zeolite catalyst were involved in the combustion process. The incorporation of Pt promoted the oxygen adsorption of the resultant catalyst. Thus, Pt/H-BETA produced 50% conversion of DCM at 350 °C, while pure H-BETA required a temperature increase to 380 °C. On the other hand, Pt/H-BETA achieved 50% TCE conversion at 400 °C, whereas the protonic zeolite needed a minimum temperature of 450 °C to attain the same conversion level. This temperature difference revealed the importance of the presence of platinum as a catalytic agent for TCE destruction. As can be deduced from activity results from both non-catalysed and catalysed experiments, TCE appeared to be a more stable compound when compared to DCM, the latter requiring higher temperatures for a given conversion level [26].

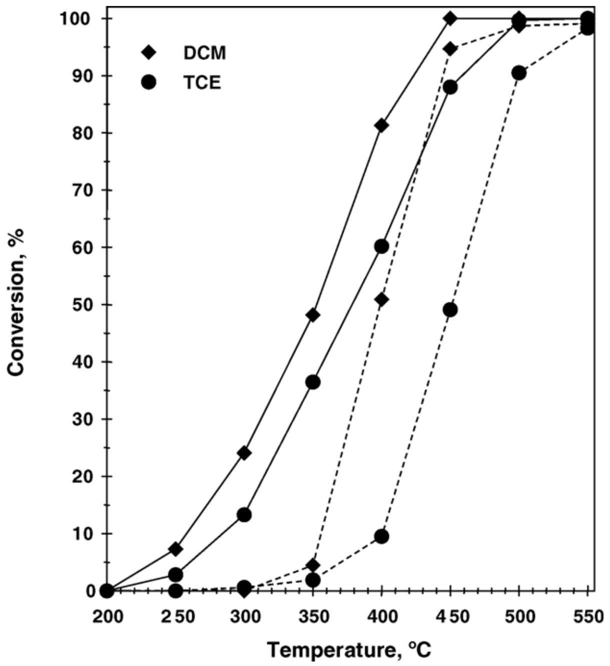

Fig. 2. Light-off curves of the combustion of DCM and TCE over Pt/H-BETA (solid lines) and H-BETA (dashed line) under dry conditions.

In addition to analysing the catalytic behaviour in chlorinated VOC destruction, the product distribution of the two H-BETA zeolite-based catalysts were also compared and discussed in terms of the characteristics of each catalyst and of the chemical nature of each chlorinated feed. Note that high conversion is not the only criterion for determining good chlorocarbon destruction catalysts. Indeed, transformation of converted carbons and chlorine atoms to carbon monoxide and molecular gas chlorine, which are toxic air pollutants, has been a common problem for most catalytic systems for total oxidation of chlorinated hydrocarbons. The primary decomposition products were carbon dioxide, carbon monoxide, hydrogen chloride and molecular chlorine over the zeolite catalysts. Moreover, decomposition of DCM and TCE also gave rise to the formation of variable amounts of methyl chloride and tetrachloroethylene at mild temperatures (300–450 °C, respectively). Tables 2 and 3 show selectivity values as a function of the temperature for DCM and TCE combustion, respectively, under dry and humid conditions. Each product selectivity was calculated on the basis of chlorine or carbon atoms present in that product divided by the total chlorine or carbon atoms present in all the product spectrum (expressed as %).

Table 2
Selectivity values towards C-containing and Cl-containing products in the combustion of DCM under dry and humid conditions over H-BETA and Pt/H-BETA catalysts

	Pt/H-BETA					H-BETA				
	350 °C	400 °C	450 °C	500 °C	550 °C	350 °C	400 °C	450 °C	500 °C	550 °C
Dry conditions										
Cl-products										
S_{HCl}[a] (%)	69.6	79.0	62.8	58.4	37.1	63.4	78.6	91.0	89.8	65.8
$S_{\mathrm{Cl_2}}$[b] (%)	1.1	12.2	34.0	41.6	62.9	0.0	0.0	1.7	3.2	34.2
$S_{\mathrm{CH_3Cl}}$[c] (%)	29.3	8.8	3.2	0.0	0.0	36.6	21.4	7.3	0.0	0.0
C-products										
$S_{\mathrm{CO_2}}$[d] (%)	42.9	73.0	100	100	100	6.2	12.9	19.4	56.1	79.8
S_{CO}[e] (%)	0.0	0.0	0.0	0.0	0.0	54.2	65.8	72.3	43.9	21.2
$S_{\mathrm{CH_3Cl}}$[f] (%)	57.1	17.0	0.0	0.0	0.0	39.6	21.3	8.3	0.0	0.0
Humid conditions										
Cl-products										
S_{HCl}[a] (%)	100	98.0	98.3	91.9	79.6	66.1	79.6	92.9	100	99.3
$S_{\mathrm{Cl_2}}$[b] (%)	0.0	2.0	1.7	8.1	20.4	0.0	0.0	0.0	0.0	0.7
$S_{\mathrm{CH_3Cl}}$[c] (%)	0.0	0.0	0.0	0.0	0.0	28.7	21.1	6.9	0.0	0.0
C-products										
$S_{\mathrm{CO_2}}$[d] (%)	100	100	100	100	100	25.8	35.3	54.9	72.8	93.2
S_{CO}[e] (%)	0.0	0.0	0.0	0.0	0.0	74.2	64.7	45.1	27.2	6.8
$S_{\mathrm{CH_3Cl}}$[f] (%)	0.0	0.0	0.0	0.0	0.0	28.7	21.1	6.9	0.0	0.0

[a] $S_{\mathrm{HCl}} = [\mathrm{HCl}]/([\mathrm{HCl}] + 2[\mathrm{Cl_2}] + [\mathrm{CH_3Cl}])$.
[b] $S_{\mathrm{Cl_2}} = 2[\mathrm{Cl_2}]/([\mathrm{HCl}] + 2[\mathrm{Cl_2}] + [\mathrm{CH_3Cl}])$.
[c] $S_{\mathrm{CH_3Cl}} = [\mathrm{CH_3Cl}]/([\mathrm{HCl}] + 2[\mathrm{Cl_2}] + [\mathrm{CH_3Cl}])$.
[d] $S_{\mathrm{CO_2}} = [\mathrm{CO_2}]/([\mathrm{CO_2}] + [\mathrm{CO}] + [\mathrm{CH_3Cl}])$.
[e] $S_{\mathrm{CO}} = [\mathrm{CO}]/([\mathrm{CO_2}] + [\mathrm{CO}] + [\mathrm{CH_3Cl}])$.
[f] $S_{\mathrm{CH_3Cl}} = [\mathrm{CH_3Cl}]/([\mathrm{CO_2}] + [\mathrm{CO}] + [\mathrm{CH_3Cl}])$.

Table 3
Selectivity values towards C-containing and Cl-containing products in the combustion of TCE under dry and humid conditions over H-BETA and Pt/H-BETA catalysts

	Pt/H-BETA					H-BETA				
	350 °C	400 °C	450 °C	500 °C	550 °C	350 °C	400 °C	450 °C	500 °C	550 °C
Dry conditions										
Cl-products										
S_{HCl}[a] (%)	50.3	48.1	40.1	31.8	20.3	95.5	79.2	63.9	44.5	32.3
$S_{\mathrm{Cl_2}}$[b] (%)	28.6	10.9	47.7	67.8	79.6	0.0	0.0	3.7	49.5	66.9
$S_{\mathrm{C_2Cl_4}}$[c] (%)	21.1	41.0	12.2	0.4	0.1	4.5	20.8	32.4	6.0	0.8
C-products										
$S_{\mathrm{CO_2}}$[d] (%)	67.8	60.9	97.2	99.5	99.8	30.4	31.9	38.8	53.7	72.1
S_{CO}[e] (%)	0.0	0.0	0.0	0.0	0.0	68.1	61.4	49.5	42.7	27.4
$S_{\mathrm{C_2Cl_4}}$[f] (%)	32.2	39.1	12.8	0.5	0.2	1.5	6.7	11.7	3.6	0.4
Humid conditions										
Cl-products										
S_{HCl}[a] (%)	94.2	88.8	79.7	76.4	73.9	99.0	98.8	98.5	98.9	99.2
$S_{\mathrm{Cl_2}}$[b] (%)	0.0	1.2	11.1	19.1	25.8	0.0	0.0	0.0	0.0	0.3
$S_{\mathrm{C_2Cl_4}}$[c] (%)	5.8	10.0	9.2	4.5	0.3	1.0	1.2	1.5	1.1	0.5
C-products										
$S_{\mathrm{CO_2}}$[d] (%)	98.9	98.3	97.3	98.6	99.9	28.3	34.7	43.7	65.8	90.6
S_{CO}[e] (%)	0.0	0.0	0.0	0.0	0.0	71.5	65.0	55.8	33.7	9.1
$S_{\mathrm{C_2Cl_4}}$[f] (%)	1.1	1.7	2.7	1.4	0.1	0.2	0.3	0.5	0.5	0.3

[a] $S_{\mathrm{HCl}} = [\mathrm{HCl}]/([\mathrm{HCl}] + 2[\mathrm{Cl_2}] + 4[\mathrm{C_2Cl_4}])$.
[b] $S_{\mathrm{Cl_2}} = 2[\mathrm{Cl_2}]/([\mathrm{HCl}] + 2[\mathrm{Cl_2}] + 4[\mathrm{C_2Cl_4}])$.
[c] $S_{\mathrm{C_2Cl_4}} = 4[\mathrm{C_2Cl_4}]/([\mathrm{HCl}] + 2[\mathrm{Cl_2}] + 4[\mathrm{C_2Cl_4}])$.
[d] $S_{\mathrm{CO_2}} = [\mathrm{CO_2}]/([\mathrm{CO_2}] + [\mathrm{CO}] + 2[\mathrm{C_2Cl_4}])$.
[e] $S_{\mathrm{CO}} = [\mathrm{CO}]/([\mathrm{CO_2}] + [\mathrm{CO}] + 2[\mathrm{C_2Cl_4}])$.
[f] $S_{\mathrm{C_2Cl_4}} = 2[\mathrm{C_2Cl_4}]/([\mathrm{CO_2}] + [\mathrm{CO}] + 2[\mathrm{C_2Cl_4}])$.

Methyl chloride generation was more noticeable over H-BETA with a peak concentration of 190 ppm at 350 °C. In contrast, the yield of this by-product was significantly inhibited with Pt/H-BETA, resulting in a maximal concentration of 95 ppm at 350 °C. This chlorinated compound was decomposed at temperatures higher than 450 °C. With regard to tetrachloroethylene formation in TCE combustion, a completely different pattern was observed. Hence, the peak concentration of this by-product, which is more toxic and recalcitrant than the starting material, was 80 ppm over H-BETA at 450 °C but increased to almost 300 ppm with Pt/H-BETA. This compound was decomposed at 500–550 °C. The formation of tetrachloroethylene was attributed to the activity of noble metals in chlorination reactions [27]. Similarly, several studies have reported a substantial chlorination of TCE to yield tetrachloroethylene over noble metal based catalysts [28,29].

The Cl analysis did not yield a satisfactory chlorine balance, but it did give a good indication of the selectivity to HCl. Dichloromethane contains sufficient hydrogen in the molecule itself to form the stoichiometric HCl exclusively. However, noticeable quantities of molecular chlorine were detected above 450 °C, and its formation increased as the temperature increased. As mentioned before, the production of chlorine is not environmentally desirable, since HCl is less toxic and can easily be removed from the effluent stream with a caustic solution. The formation of Cl_2 was attributed to the occurrence of the Deacon reaction, whereby HCl and oxygen are converted to Cl_2 and water ($2HCl + (1/2)O_2 \rightleftharpoons Cl_2 + H_2O$). The relatively low concentration of this compound (<200 ppm) detected at 550 °C with H-BETA was attributed to the involvement of surface OH groups that partially reacted with chlorine to yield hydrogen chloride [17,30]. In contrast, the combustion of DCM catalysed by non-acidic (Table 1) SiO_2 gave rise to 400 ppm of Cl_2 at 550 °C. Cl_2 yield via the Deacon reaction was promoted with the incorporation of platinum, since the selectivity to this by-product at 550 °C increased from 34% over H-BETA to 63% over Pt/H-BETA (Table 2). Unlike DCM, TCE contains more chlorine atoms than hydrogen atoms, and as a result Cl_2 is formed in the absence of water. When TCE complete conversion was attained (550 °C), 1300 ppm pf Cl_2 were detected in the product spectrum over Pt/H-BETA catalyst. Since there was not enough chlorine present in TCE to account for the observed quantities of Cl_2 (the stoichiometric amount would be 1000 ppm), the Deacon reaction would be contributing to the promotion of the generation of this by-product. As in the case of DCM oxidation, when oxidising TCE the metal loaded zeolite catalyst showed greater values of Cl_2 formation than the protonic zeolite. Thus, Cl_2 selectivity values at 550 °C increased from 40% with H-BETA to 80% with Pt/H-BETA (Table 2). It is worth pointing out that although H-BETA was less active than Pt/H-BETA, the former catalyst showed the advantage of a considerably higher selectivity to HCl, the preferred chlorinated deep oxidation product.

As for the formation of carbon oxides, it must be indicated that carbon monoxide was the primary product over H-BETA. In spite of the fact that the yield of carbon dioxide increased with increasing temperature, CO_2 selectivity at 500 °C was as low as 50–60% (Table 2). CO homogenous oxidation appreciably took place at 550 °C, and CO_2 selectivity markedly increased. The remarkable formation of CO during chlororganics combustion has been reported for other protonic zeolites as well as for blank supports such as Al_2O_3, ZrO_2, and SiO_2 [31]. However, the addition of platinum to the zeolite support shifted the CO_2 selectivity to around 100%, eliminating the presence of CO in the effluent stream (Table 2). This proved that platinum efficiently served the role of oxidising CO to CO_2 [32]. An increase in CO_2 production over the platinum system was evident for the destruction of both chlorocarbons. Carbon balances closed to 90–100% in the temperature range investigated. No propensity for both DCM and TCE to form coke was found.

3.3. *Catalytic performance under humid conditions*

Catalytic runs were also conducted under humid conditions, since water is present in significant quantities in effluent streams containing chlorocarbons. The presence of water in the gaseous stream can have significant effects on the destructive properties of the catalysts and on the product distribution. The concentration of water vapour in a gas effluent stream can easily exceed the concentration of chlorinated VOCs. In the case of streams from air stripping in contaminated groundwater, the water concentration can be higher than 10,000 ppm. In this study a water concentration of 15,000 ppm has been used.

Fig. 3 shows the evolution of conversion of 1000 ppm chlorinated VOC at varying temperatures over the zeolite catalysts under humid conditions. The effect of the presence of water on catalytic activity was observed to depend on the type of catalyst. Hence, when using H-BETA as a catalyst, conversion was considerably inhibited, mainly at low temperatures, and the extent of the decrease therefore became less appreciable with increasing temperature. The temperature for 50% conversion increased to 405 and 470 °C for DCM and TCE, respectively. This behaviour evidenced a competitive adsorption mechanism between VOC molecules and water molecules [19]. Previous results had indicated that the catalytic activity of aluminium-rich H-zeolites such as H-Y and H-MOR were more affected by the addition of water due to their hydrophilic character [15]. Interestingly, a considerable improvement in conversion was noted for Pt/H-BETA in the presence of 15,000 ppm of water. Thus, T_{50} value in DCM combustion decreased from 350 °C under dry conditions to 315 °C under humid conditions. Analogously, T_{50} value in TCE combustion decreased from 400 °C in the absence of water to 375 °C in the presence of water. This promoted conversion was associated with the efficient removal of chlorine species by water for the catalyst surface

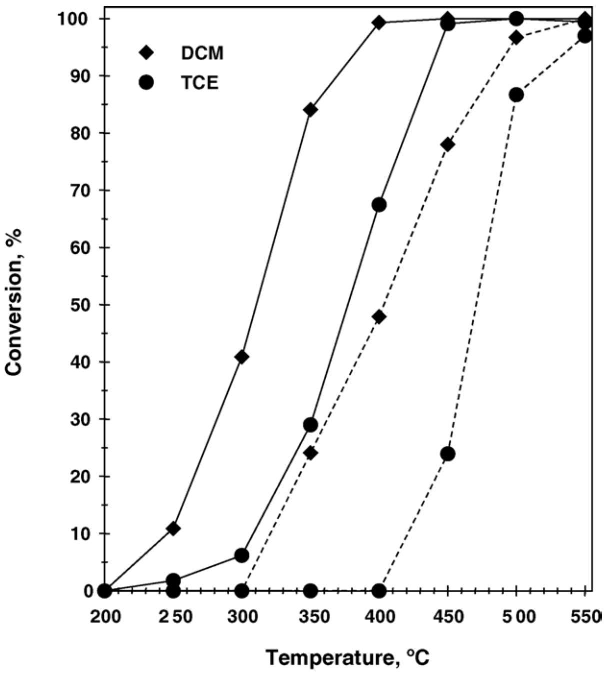

Fig. 3. Light-off curves of the combustion of DCM and TCE over Pt/H-BETA (solid lines) and H-BETA (dashed line) under humid conditions.

[33]. It is suggested that chlorine species remain on the catalyst metallic surface after reaction, hindering further adsorption by occupying the catalytic sites. The hydrogen content of water was found to play a key role in cleaning these species from the active sites – as HCl – rendering them to the reactant molecules, while on the blank support it can only block adsorption sites [34]. As regards the relative reactivity of the chlorinated VOCs, it was noted that the addition of water vapour did not alter the trend observed in the dry runs.

As well as resulting in enhanced catalytic activity, the presence of water in the feed stream also had a remarkable effect on reaction product distribution [35]. On one hand, the presence of chlorinated by-products, namely methyl chloride and tetrachloroethylene, decreased over both zeolite catalysts. Hence, reduced amounts of methyl chloride (10 ppm) and tetrachloroethylene (70 ppm) were detected with Pt/H-BETA under humid conditions. On the other hand, upon adding 15,000 ppm of water to the feed stream, virtually no molecular chlorine was detected in the combustion of both chlorinated feeds over H-BETA with HCl selectivity values higher than 99% (Table 3). In contrast, Cl_2 generation was not completely inhibited with Pt/H-BETA, since appreciable amounts were still detected under humid conditions. Hence, HCl selectivity at 550 °C increased to 80 and 74% in DCM and TCE combustion, respectively (Table 3). It is thought that water could inhibit the Deacon reaction, and provided the hydrogen required for the formation of the desired product [36]. This was especially relevant for TCE, a hydrogen-lean reactant. It is known that hydrogen-rich additives are required to improve selectivity to HCl in the combustion of this type of chlorinated feeds [5]. The limited Cl_2 concentration under humid conditions further reduced the likelihood of the second reaction between TCE and Cl_2 to form tetrachloroethylene [37]. Additionally, the presence of water caused a significant shift of the product selectivity towards CO_2 over H-BETA [18]. The above-mentioned observations clearly demonstrate the presence of water in the feed stream in the combustion of DCM, and TCE influenced the process in a beneficial manner.

A comparison of the results shown in this study with other supported Pt catalysts (Pt/Al_2O_3) proves that the support plays a relevant role in determining the catalytic behaviour of the platinum catalyst, since Pt/H-BETA was noticeably more active [8]. On the other hand, when comparing the catalytic performance of the Pt/H-BETA catalyst with that of the PdO/H-BETA recently published [19], it was noticed that the former was significantly less active in the combustion of DCM and TCE. As regards product selectivity, both noble metal zeolite catalysts led to the yield of a comparable amount of trichloroethylene. Unlike H-BETA, the formation of methyl chloride was not detected over noble metal catalysts. The Pt/H-BETA zeolite showed the advantage of a remarkably higher selectivity to deep oxidation products (HCl and CO_2). Furthermore, it was found that the addition of water resulted in a more noticeably promoted conversion, this indicating that this hydrogen-rich additive was more efficient for the removal of chlorine species from the active sites in platinum catalysts supported on H-BETA zeolite.

Elemental analysis of the spent catalysts qualitatively indicated significant Cl contents for samples tested in the absence and the presence of water. Moreover, N_2 adsorption measurements and XRD analysis of the used zeolite catalysts showed a partial collapse of the crystalline structure, which was related to dealumination of the zeolite with the HCl formed during catalytic oxidation. This deactivating effect is more noticeable for the catalysts investigated under humid conditions. A study on the deactivation of the zeolite catalysts in the combustion of chlorinated VOCs under both dry and humid conditions is currently in progress.

4. Conclusions

The catalytic combustion of selected chlorinated VOCs, namely dichloromethane and trichloroethylene, over blank H-BETA and Pt/H-BETA zeolite catalysts was comparatively studied under dry and humid conditions so as to analyse the role of platinum on catalytic activity and product selectivity.

By comparing the chlorinated VOC conversion using Pt/H-BETA and only the support material, H-BETA, it was clear that Pt reduced the destruction temperatures, although H-BETA was active owing to its distinct acidic properties. However, with H-BETA only, CO production was much higher. The addition of platinum improved this point, but created two new problems: the concomitant production of molecular chlorine and highly chlorinated by-products, such as tetrachloroethylene in TCE combustion.

The presence of an excess of water in the gaseous stream exhibited substantial beneficial effects on the performance of the noble metal zeolite catalyst. Hence, catalytic conversion was significantly promoted, since water acted as an efficient cleaning agent of chlorine species from the surface of the catalyst. Furthermore, the addition of water was also important for producing the desired HCl rather than Cl_2 as a product from the combustion of chlorohydrocarbons. Likewise, the formation of tetrachloroethylene considerably decreased under humid conditions.

In short, due to its high catalytic activity and remarkable selectivity towards environmentally desirable oxidation products under humid conditions, the Pt/H-BETA catalyst examined herein appears to be suitable for low-temperature chlorohydrocarbon emission control.

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