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Dealuminated Y Zeolites for Destruction of Chlorinated Volatile Organic Compounds

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Chemical dealumination by $(NH_4)_2SiF_6$ treatment has been investigated as an effective method for improving the catalytic behaviour of Y zeolites for chlorinated hydrocarbon combustion. Hence, the deep catalytic oxidation of dichloromethane (DCM), 1,2-dichloroethane (DCE), and trichloroethylene (TCE) was evaluated over two Y zeolites with different Si/Al ratios, at conditions of lean chlorocarbon concentration (around 1000 ppm) in dry and humid (15,000 ppm of water) air between 200 and 550°C. Catalyst-subjected to dealumination exhibited a higher activity in CVOC oxidation compared with that of the untreated one. The activity increase was attributed to the strong Brønsted acidic sites formed during catalyst dealumination. The ease of destruction was found to decrease in the following order: DCE > DCM > TCE. The main oxidation products formed were CO, CO_2, HCl, and Cl_2. In addition, some other chlorinated by-products/intermediates were detected, namely vinyl chloride, methyl chloride, and tetrachloroethylene in the oxidation of DCE, DCM, and TCE, respectively. The addition of water slightly diminished the zeolite activity and markedly changed the product distribution. Hence, by-product generation was found to be significantly reduced. Water also promoted somewhat the CO_2 selectivity and led to complete reaction of chlorine to HCl by the Deacon reaction. © 2002 Elsevier Science (USA)

Key Words: **chlorinated volatile organic compounds; CVOCs; 1,2-dichloroethane; dichloromethane; trichloroethylene; catalytic destruction; Y zeolite; dealumination; ammonium hexafluorosilicate.**

INTRODUCTION

Chlorinated volatile organic compounds (CVOCs), such as dichloromethane (DCM), 1,2-dichloroethane (DCE), and trichloroethylene (TCE), are a wide-ranging class of solvents commonly found in industrial waste streams and they constitute a major source of air and groundwater pollution (1). Among the available waste disposal processes, catalytic oxidation may be the most economically advantageous method for dilute chlorocarbon destruction because of its low temperature of operation, low energy consumption, and reduction of noxious by-product formation such as PCDFs, PCDDs and NO_x (2).

We have previously found (3, 4) that various commercial H–zeolites (H–Y, H–ZSM-5, and H–MOR) showed a high activity in the oxidative destruction of 1,2-dichloroethane and trichloroethylene in the absence and in the presence of water vapour, which was directly associated with the presence of strong Brønsted acidity. It must be noted from these studies that the H–Y sample was found to a present moderate activity for CVOC conversion owing to the lack of appropriate catalytic sites, i.e., Brønsted acid sites of high strength.

The modification of the acidic properties and resultant catalytic properties through dealumination of zeolite lattices by various treatments has therefore been a matter of considerable interest (5, 6). In the present study, an H–Y zeolite was dealuminated via the procedure described by Skeels and Breck (7) using $(NH_4)_2SiF_6$ under closely controlled conditions. The scope of this work was to analyse the effect of chemical dealumination on the catalytic performance of a commercial H–Y zeolite in the oxidative decomposition of several chlorinated hydrocarbons (DCM, DCE, and TCE) in air, at lean concentration conditions (around 1000 ppm) between 200 and 550°C. Additionally, the effect of water (15,000 ppm) on conversion and product distribution has also been investigated, as the flue gas streams usually carry a significant moisture content in industrial applications.

EXPERIMENTAL AND METHODS

Materials and Catalyst Characterisation

The zeolite Y (CBV400) in its H-form (H–Y) was supplied from Zeolyst Corp. and used as received. Its dealuminated form, H–Y(d), was prepared as follows. The starting material was obtained by two successive ion exchanges with a 3 M ammonium nitrate solution of the commercial H–Y sample at room temperature for 24 h in order to reduce the sodium content. Then, the NH_4H–Y zeolite was preheated in a 0.5 M ammonium acetate solution at 80°C. An aqueous solution of ammonium hexafluorosilicate was added dropwise at a rate of 50 $cm^3\ h^{-1}$ under vigorous stirring. The $(NH_4)_2SiF_6$-to-zeolite ratio was adjusted to remove

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50% of the aluminium in the zeolite structure. Afterwards, the temperature was raised to 95°C and kept at this temperature for 3 h. Finally, the zeolite was recovered by filtration and repeatedly washed with hot deionised water to remove the unreacted $(NH_4)_2SiF_6$ completely. The zeolites were pelletised using methylcellulose as a temporary binder which was removed by calcination at 550°C in air. Then the pellets were crushed and sieved to grains of 0.3–0.5 mm in diameter and used for catalytic runs without further activation.

The BET surface areas of the zeolite samples were determined by N_2 adsorption–desorption at −196°C in a Micromeritics ASAP 2010 equipment. The compositions were determined using a Philips PW 1480 X-ray fluorescence (XRF) spectrometer. The X-ray powder diffraction (XRD) patterns were obtained with a Philips PW 1710 X-ray diffractometer with Cu$K\alpha$ radiation. The characterisation of the acidic properties of the Y zeolites was performed by temperature-programmed desorption (TPD) of ammonia and the adsorption of pyridine followed by diffuse reflectance infrared spectroscopy (DRIFTS). Experimental procedures are described in detail elsewhere (3).

Catalytic Activity Measurement

Oxidation reactions were carried out in a conventional fixed-bed reactor under atmospheric pressure (8). 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}. The feed stream to the reactor was prepared by delivering the liquid chlorinated hydrocarbon (1000 ppm) and water (15,000 ppm) by two syringe pumps into dry air, which was metered by a mass flow controller. Details about the experimental procedure for reaction product analysis are described elsewhere (8).

RESULTS AND DISCUSSION

Catalyst Characterisation

The main physicochemical properties of the two catalysts tested are given in Table 1. The crystallinity of the dealuminated sample was determined on the basis of the nine most intense X-ray reflections, considering the crystallinity of the parent H–Y as 100%. The unit cell parameter, a_0, was calculated following the ASTM method (D-4938-85). The Si/Al framework ratio was deduced from the value of the unit cell parameter a_0 using the equation given by Fichtner–Schmittler *et al.* (9). This empirical equation has been used in several papers dealing with Y zeolites dealuminated by ammonium hexafluorosilicate treatment (10, 11).

For the parent material XRF analysis gave aluminium contents that were noticeably larger than the framework aluminium (FAL) concentration, indicating the presence of large amounts of extraframework or nonframework aluminium (EFAL). These observations were also confirmed by infrared spectroscopy of the zeolite hydroxyl region. Indeed, this high EFAL content (about 40% of the total aluminium content) is similar to that of ultrastable Y zeolites, which are known to present notable amounts of these type of aluminium species. Chemical analysis of the extracted sample indicated that the ammonium hexafluorosilicate extraction removed 50% of the total aluminium from the zeolite. Table 1 indicates that almost 100% EFAL and 30% FAL were removed from the parent material.

It was seen that as the Si/Al framework ratio increased, the unit cell size of $(NH_4)_2SiF_6$-treated sample contracted due to the smaller size of aluminium atoms (12). Certainly, it was found for this sample that the framework Si/Al ratio obtained from the unit cell size value was very close to the bulk Si/Al ratio obtained by XRF analysis. On the other hand, XRD measurements indicated no observable reduction in crystallinity of the dealuminated zeolite. Moreover, no impurities were detected in the structure (13). Accordingly, the textural properties of the dealuminated sample were not changed with respect to those of the parent material.

Figure 1 shows the diffuse-reflectance infrared spectra of pyridine adsorbed on the zeolites at 200°C in the region 1700–1400 cm^{-1} at 1.33 $N\ m^{-2}$. The absorption band around 1545 cm^{-1} is assumed to be characteristic for pyridinium ions adsorbed on Brønsted sites, while absorption bands at 1450 cm^{-1} are attributed to coordinatively adsorbed pyridine on Lewis sites (14). H–Y possesses a large number of both types of acid sites with a ratio of Brønsted to Lewis acid sites, measured as the ratio of the integrated areas of the respective pyridine bands, of 0.8. By contrast, a smaller band at 1450 cm^{-1} was noted for the H–Y(d) sample, indicating that the dealumination treatment led to a sample with very few Lewis sites (15).

TABLE 1

Chemical Composition ($(Si/Al)_{bulk}$), Total Al Content per Unit Cell (Al_{total}), Framework Al Content per Unit Cell ($Al_{fram.}$), Extraframework Al Content per Unit Cell ($Al_{extraf.}$), Unit Cell Size (a_0), Crystallinity, BET Surface Area (S_{BET}), and Pore Volume (V_{pore}) of Y Zeolites

	$(Si/Al)_{bulk}$	$(Si/Al)_{fram.}$	Al_{total}	$Al_{fram.}$	$Al_{extraf.}$	a_0 (Å)	Crystal. (%)	S_{BET} ($m^2\ g^{-1}$)	V_{pore} ($cm^3\ g^{-1}$)
H–Y	2.6	4.9	53.3	32.2	21.1	24.52	100	900	0.382
H–Y(d)	6.2	6.5	26.7	25.5	1.2	24.46	95	820	0.334

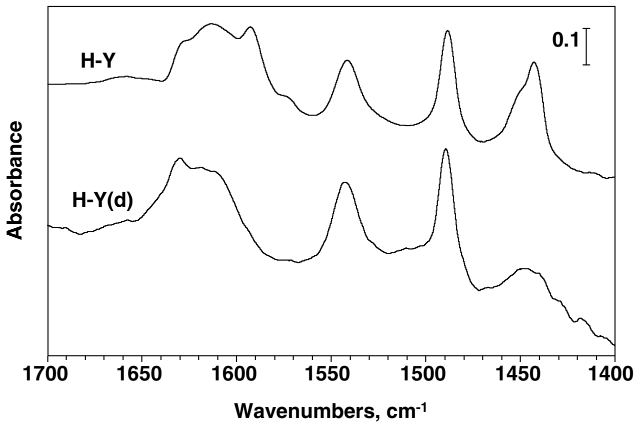

FIG. 1. Difference diffuse-reflectance infrared spectra of chemisorbed pyridine on Y zeolites at 200°C.

The amount of adsorbed ammonia at 100°C was 0.65 and 0.48 mmol g^{-1} for the H–Y and H–Y(d) samples, respectively, thereby showing an overall loss in the total number of acid sites with dealumination (16). As can be seen in the NH_3-TPD graphs (Fig. 2), both TPD profiles displayed a major desorption peak around 150°C. This peak is indicative of the weak (Brønsted and/or Lewis) sites present in the zeolite catalysts (17). It was found that the apparent number of weak sites was larger in H–Y (around 75% of the total acid sites) in comparison with H–Y(d) (around 55% of the total acid sites). A second smaller desorption peak with maximum at 300°C was obtained for H–Y(d), indicating the presence of strong Brønsted acid sites. On the contrary, H–Y showed almost no inflection in this region. This could be explained by noting that following dealumination, the aluminium atoms in the zeolite structure were partially replaced by silicon atoms, which increases the spacing between neighbouring aluminium atoms, further strengthening the remaining Brønsted sites. Hence, the $(NH_4)_2SiF_6$ dealumination process modified not only the number of the acid sites of the zeolites but also their acid strength distribution.

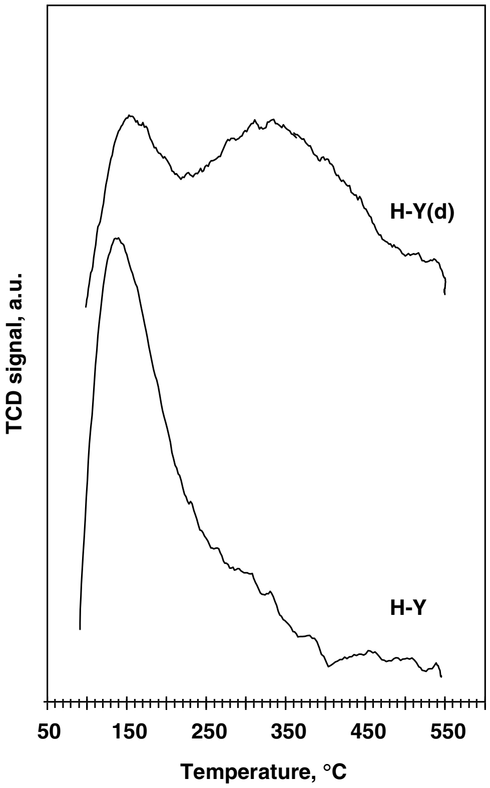

FIG. 2. Acidity of Y zeolites determined by temperature-programmed desorption of ammonia.

Catalytic Activity Results

Figure 3 shows the conversion of DCE, DCM, and TCE over both Y zeolite catalysts as a function of temperature. Both Y zeolites exhibited a high activity for the oxidative destruction of CVOCs, with H–Y(d) being more active. Comparing the lights-off curves, it was found that the ease of destruction decreased in the following order: DCE > DCM > TCE. Thus, H–Y(d) showed a T_{50} (temperature at which 50% conversion is achieved) value of 270°C for DCE decomposition and a T_{90} (temperature at which 90% conversion is achieved) of 320°C compared with those obtained with H–Y zeolite, i.e., 325 and 380°C. As regards DCM, the H–Y(d) sample produced over 50% conversion at 345°C. This represents about a 25°C drop in reaction temperature for similar conversion levels as compared to the H–Y catalyst. The difference in activity between both catalysts for 90% conversion was larger, as H–Y(d) needed

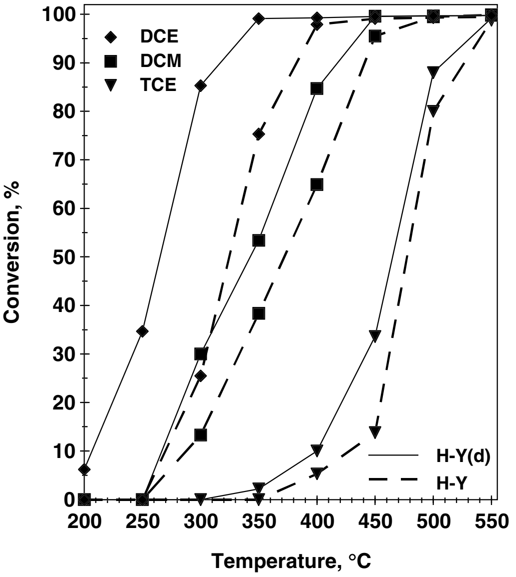

FIG. 3. Conversion of 1,2-dichloroethane (DCE), dichloromethane (DCM), and trichloroethylene (TCE) on Y zeolites vs reaction temperature under dry conditions.

400°C while H–Y required 455°C. In contrast, almost no significant conversion of TCE could be obtained at temperatures below 450°C. Hence, the T_{50} value of H–Y(d) was 465°C compared to 480°C obtained over H–Y, and complete conversion (90%) was attained at 500°C over H–Y(d) whereas a minimum temperature of 525°C was required by H–Y zeolite. Therefore, the improvement in catalytic activity due to chemical dealumination was found to be larger for DCE than for DCM and TCE.

The highly active performance for H–Y(d) in CVOC conversion may be accounted for by the generation of new strong Brønsted sites due to the dealumination treatment. Hence, a medium with a modest concentration of Brønsted sites which were primarily of high acid strength proved to be effective for catalytic purposes. It is well accepted that Brønsted acidity plays a key role in determining the activity of acidic catalysts since the oxidation of chlorinated hydrocarbons is initiated by the adsorption of the hydrocarbons on these sites (18).

Product Distribution of CVOC Decomposition

The main oxidation products formed during CVOC destruction were CO, CO_2, HCl, and Cl_2 over both zeolites. In addition, some other chlorinated by-products/intermediates were detected, namely vinyl chloride, methyl chloride, and tetrachloroethylene in the oxidation of DCE, DCM, and TCE, respectively. The presence of vinyl chloride suggested that the abstraction of HCl (dehydrochlorination) was the first step in the DCE conversion between 250 and 400°C (19). Vinyl chloride (CV), being stable, did not undergo further dehydrochlorination and oxidised to CO, CO_2, and HCl above 450°C (Fig. 4). The vinyl chloride peak concentration over H–Y was around 860 ppm while H–Y(d) yielded a smaller amount of this reaction intermediate (about 660 ppm). As for DCM, it was noted that methyl chloride (CM) was formed at mild temperatures as a result of the hydrodechlorination of the feed molecule (20). H–Y(d) was found to be slightly more selective to this by-product than H–Y. Thus, 325 ppm was measured with H–Y(d) whereas 190 ppm was generated over H–Y. At high temperatures CO and HCl were the major products along with small amounts of CO_2 (20).

DCE and DCM contain sufficient hydrogen atoms for the complete oxidation to the desired HCl. However, small traces of chlorine were detected only at high temperatures (>500°C) due to the occurrence of the Deacon reaction ($2HCl + 1/2O_2 \rightleftharpoons Cl_2 + H_2O$), with selectivity values to this hazardous by-product lower than 10%. In contrast to the results reported for metal-loaded catalysts (8), the low Cl_2 selectivity of H-type zeolites indicated that the Deacon reaction occurred over these catalysts to a very reduced extent (3).

When decomposing TCE no significant activity was measured below 350°C. As the temperature exceeded 400°C, the conversion rapidly increased and CO, CO_2, HCl, and Cl_2 yields were promoted in quantity. Small amounts of tetrachloroethylene (PER) (around 235 ppm over H–Y(d) and about 150 ppm over H–Y) were also produced by the chlorination of the feed molecule (21). It is worth noting that hydrogen chloride and chlorine were not generated in an equimolecular ratio when TCE was completely decomposed, as would be expected according to the stoichiometry. It is thought that the zeolite hydroxyls in the structure largely promoted HCl formation by the Deacon reaction (22). Therefore, the acid character of the zeolites appeared to be a favourable property to enhance HCl selectivity, mainly in the combustion of compounds with a low H/Cl ratio.

As far as CO_2 formation was concerned, there was observed a moderate selectivity to this deep oxidation product, resulting in values ranging from 40 to 65%. This behaviour reflected the difficulty of CO oxidation over protonic Y zeolites and, in general, over acidic catalysts not modified with an active metal for CO oxidation (23).

Influence of Water on the Catalytic Activity and Product Distribution

Figure 4 shows the lights-off curves of the CVOC oxidation carried out under humid conditions (dashed lines). It was noticed that the addition of water (15,000 ppm) to the feed stream did not alter the order of activity observed in the dry runs (solid lines). An average increase in T_{50} values about 20°C was measured, suggesting that water played an inhibiting role in the decomposition reaction (18, 24). This inhibition probably reflected the competition of the reactant molecules with water molecules for adsorption on the active sites.

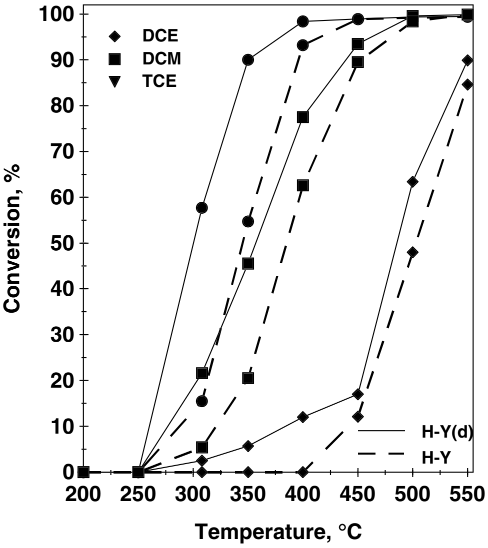

FIG. 4. Conversion of 1,2-dichloroethane (DCE), dichloromethane (DCM), and trichloroethylene (TCE) on Y zeolites vs reaction temperature under humid conditions (15,000 ppm H_2O).

The presence of water in the CVOC oxidative destruction changed markedly the reaction product distribution (Fig. 5). Product distribution under humid conditions was comparable, as vinyl chloride, methyl chloride, and tetrachloroethylene were produced as intermediates/by-products, but in a noticeably reduced amount with respect to those observed under dry conditions. The inhibiting effect of water on the formation of reaction intermediates was consistent with previous works dealing with the oxidation of CVOCs (25). Likewise, the presence of water vapour greatly lowered the production of molecular chlorine in favour of increasing hydrogen chloride formation with 100% selectivity values (25). On the other hand, water addition also resulted in an important decrease in CO formation, leading to a substantial improvement in CO_2 generation, with selectivity values around 70–80% (26).

Carbon balances were typically greater than 90% for DCM and TCE decomposition runs. Nevertheless, due to coke deposition carbon balances were within 80–90% when oxidising DCE at temperatures between 200 and 450°C (27). As a result, carbon balances were found to be higher than 100% at elevated temperatures due to the combustion of this coke. However, unlike DCE, very low coke formation was noticed with DCM and TCE. This result could be explained by considering the simultaneous presence of a higher number of hydrogen and carbon atoms in DCE in comparison with those in DCM and TCE, which led to a noticeable coke formation during reaction. Also, the VC generated during DCE combustion was likely to polymerise inside the porous structure of the zeolites.

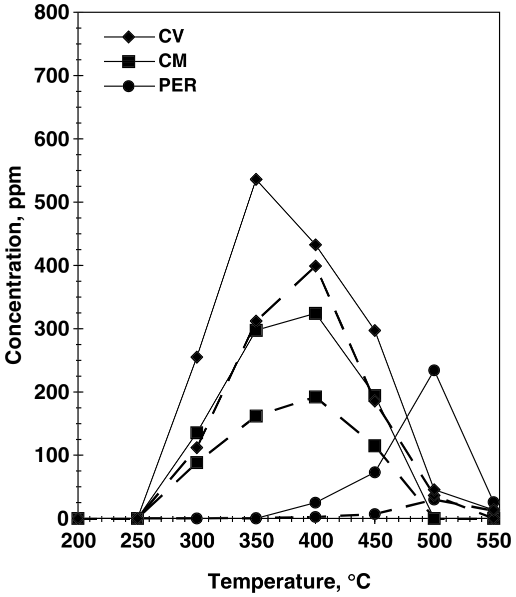

FIG. 5. Concentration profiles of chlorinated intermediates/by-products over H–Y(d) in the absence of water (solid lines) and in the presence of 15,000 H_2O (dashed lines).

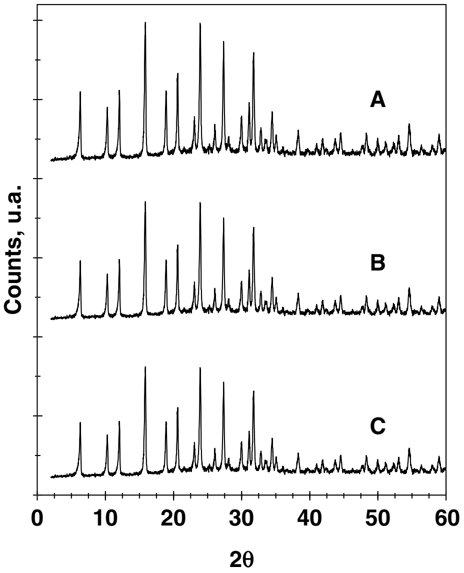

FIG. 6. X-ray diffraction patterns for H–Y(d) zeolite: (A) fresh, (B) after DCM decomposition in the absence of water, and (C) after DCM decomposition in the presence of 15,000 H_2O.

On the other hand, it is worth taking into account the fact that the chlorine balance was in the range of 75–90% under dry conditions whereas it was in the range of 65–80% in the catalytic experiments performed in the presence of water. It is known that Al–O bonds in the zeolite framework can be easily attacked by the HCl formed during reaction, leading to the formation of $AlCl_3$ that could be retained in the zeolite pellet (28). This halogen deactivation causes the partial collapse of the framework and the blockage of the porous structure and it is noticeably enhanced by the presence of water. XRD patterns of the used samples were analysed in order to study the resistance of the zeolites to dealumination, which results in a reduction of crystallinity. The crystallinity of deactivated Y zeolites diminished to 85%. A slight decrease in crystallinity (from 85 to 80%) was noticed in all the deactivated samples under humid conditions with respect to those measured for the samples tested in the absence of water. Additional NH_3-TPD experiments of the deactivated samples indicated that the total acidity of the zeolites decreased (about 8–10%) with exposure to CVOC. This confirmed a slight deactivation of Y zeolites after reaction.

CONCLUSIONS

Chemical dealumination by $(NH_4)_2SiF_6$ treatment was proven to be an effective method for enhancing the catalytic performance of H–Y zeolites for the oxidative decomposition of a variety of chlorinated compounds, namely 1,2-dichloroethane, dichloromethane, and trichloroethylene. When Y zeolite underwent dealumination the total number of acid sites was reduced but the strength of the remaining isolated acid sites, which were mostly Brønsted sites, increased. This was manifested as an increased activity for chlorinate volatile organic compound destruction.

Comparing the lights-off curves, the ease of destruction was found to decrease in the following trend: 1,2-dichloroethane > dichloromethane > trichloroethylene. The main oxidation products formed during chlorocarbon destruction were carbon monoxide, carbon dioxide, hydrogen chloride, and chlorine. In addition, some other chlorinated by-products/intermediates were detected, namely vinyl chloride, methyl chloride, and tetrachloroethylene. It is interesting that Y zeolites were highly selective to hydrogen chloride generation; nevertheless, zeolite catalysts led to considerable amounts of carbon monoxide.

It was noticed that the presence of water in the feed stream did not alter the order of reactivity observed in the dry experiments. The activity of the zeolites was reduced due to the probable competition of the reactant molecules with water molecules for adsorption on the active sites. The combustion of chlorinated compounds under humid conditions promoted the reaction towards environmentally desirable deep oxidation products (HCl and CO_2) and considerably inhibited the formation of chlorinated intermediates and by-products.

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