[Review Paper]

Hydrodechlorination over Zeolite Supported Catalysts
—Clarification of Reaction Mechanism—

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Chlorinated compounds emitted into the atmosphere are responsible for the current thinning and shrinking of the ozone layer in the stratosphere. Two main potential methods have been suggested for their transformation: oxidative destruction to form environmentally safe products or hydrodechlorination to form potentially valuable chemical compounds. In this review, performances of halogenated compounds over the zeolites and the noble metal-containing zeolite catalysts are characterized by different spectroscopic methods (IR, NMR, etc.) to clarify the reaction mechanism of hydrodechlorination over the catalysts. NMR studies provided evidence that chloro-fluorocarbon reacts more aggressively with zeolites at elevated temperatures. The extent and nature of reaction depended on the zeolite type and the exchanged cation. Infrared spectra of the gas phase showed that HCl, CO₂ and COCl₂ were detected as the reaction products in the hydrodechlorination reaction of CCl₂F₂ over HY. The phosgene intermediate is believed to be the key to the structural damage of the zeolite. Pt-containing zeolite catalyst was more active in the hydrodechlorination of carbon tetrachloride than the Pd-containing catalyst, and beside the main products (methane and HCl) chloroform as intermediate product was formed. On Pd-containing zeolite no chloroform, but high amounts of ethane as final products together with methane were formed. The activity and selectivity of the hydrodechlorination reaction of various chlorine-containing compounds (C₁, C₂, with and without fluorine content) on different metal-containing zeolites of various types is summarized.

Keywords

Hydrodechlorination, Zeolite, Noble metal, Acidity, Dealumination, IR spectroscopy

1. Introduction

Chlorinated compounds emitted into the atmosphere are responsible for the current thinning and shrinking of the ozone layer in the stratosphere. Chlorofluorocarbons were phased out by the Montreal Protocol¹⁾ and common compounds such as carbon tetrachloride are also forbidden by the Copenhagen amendment. Therefore, environmentally safe and economically valuable transformation of such materials is very important but presents a big challenge. Two main methods have been suggested: oxidative destruction to environmentally safe products (H₂O, CO₂, etc.) or transformation to potentially valuable chemical compounds (HCl, different hydrocarbons, etc.) by hydrodechlorination²⁾.

Many research groups have investigated hydrodechlorination, typically using supported noble metal catalysts. In a pioneering work, the hydrodechlorination of carbon tetrachloride was studied in the presence of Pt deposited on η -Al₂O₃ catalyst³⁾. Chloroform and

methane were produced at constant molar ratio. More recently, several catalysts have been tested. Among the catalytic metals, platinum and palladium seem to be the most important in the process of chlorine removal from organic molecules. These metals were supported on different conventional carriers such as active carbon²⁾, Al₂O₃⁴⁾, AlF₃, silica, and magnesia⁵⁾, as well as non-conventional carriers like porous glass⁶⁾.

Zeolites are also appropriate catalysts for both the oxidative decomposition^{7a),7b),8)} and the hydrodechlorination of chlorinated hydrocarbons⁹⁾. Different transition metals (for example Co), noble metals (Pt), and bimetallic forms on zeolite support are promising catalysts for hydrodechlorination^{10),11)}. Zeolites have high internal surface areas and cation exchange capacities, so the introduction of transition or noble metal catalytic function is easy. The uniform pore system allows control of the size and the dispersion of the metal. Therefore, zeolites offer a number of potential advantages as catalysts or catalyst supports over other supported metal catalysts.

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2. Experimental

Two types of zeolites were used with different Si/Al ratios for the hydrodechlorination reactions, faujasite and ZSM-5, and two methods were applied for doping with noble metals, impregnation and ion exchange. NaY-FAU (Union Carbide product) was used as the parent zeolite of the faujasite catalysts with $\text{Na}_{58}\text{Al}_{58}\text{Si}_{134}\text{O}_{384}$ unit cell composition (Si/Al = 2.3). NaY zeolite was impregnated with $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ solution and conventional ion exchange was carried out in $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$ and $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ solutions, respectively¹².

IR spectroscopic self-supporting wafer technique was used for acidity, adsorption and catalytic measurements.

The wafers (10 mg/cm²) were prepared from the powdered zeolites and placed into the sample holder of the *in-situ* IR cell. After treatment the sample was cooled to room temperature and the background spectrum of the zeolite was recorded.

For the acidity measurements, 1.33 kPa (10 Torr) of pyridine was introduced into a cell containing the pretreated self-supporting wafer and the temperature was raised to 473 K. After cooling the sample to room temperature, the spectrum of the adsorbed pyridine was measured to assess the peak areas of the bands around 1450 and 1540 cm⁻¹, characteristic of pyridine bonded to Lewis and Brønsted acid sites¹³.

To study the adsorption and reaction of chlorinated compounds, the pretreated zeolite wafers were loaded to 1.33 kPa of reactant at room temperature. Both the surface species and the gas-phase products were analysed as the reaction proceeded under various experimental conditions.

Structural changes occurring in the zeolite framework upon reaction with chlorinated compounds were investigated by the KBr pellet IR spectroscopy technique.

Multinuclear NMR (nuclear magnetic resonance) spectroscopy was performed using a Bruker MSL 400 spectrometer to obtain ²⁹Si [79.4 MHz, 4 μs ($\Theta = \pi/2$) pulse, repetition time was 6.0 s] and ²⁷Al [104.3 MHz, 1.0 μs ($\Theta = \pi/12$) pulse, repetition time was 0.2 s] spectra for all samples before and after reaction. *In-situ* ¹³C MAS NMR spectra were measured at 100.6 MHz. The zeolite samples were packed into special NMR tubes and evacuated at 723 K for 2 h. The activated zeolite samples were loaded with CCl₂F₂ (CFC-12) to the ratio of 0.01 g_{CFC}/0.05 g_{zeolite}, then the tubes were carefully sealed. Spectra were recorded after heating the tube at various temperatures.

3. Adsorption and Transformation of CFCs over Zeolites

There are numerous fundamental studies of the adsorption of various chlorofluorocarbons (CFCs) in zeo-

lites. Investigation of the adsorption of CCl₂F₂ in CsNaY-FAU zeolite by both theoretical and experimental methods concluded that the adsorption cannot be described by a normal Langmuir-type isotherm. At low pressure, the molecules adsorbed selectively on Cs⁺ ions, and at higher pressure, aggregated in the supercages of the zeolite¹⁴. The adsorption data fitted the Hill equation¹⁵. One-dimensional channel zeolite topologies, such as mordenite, may be preferred over larger and more open pore structures such as FAU for efficient adsorption of heavily halogenated molecules¹⁶.

Spectroscopic methods (FTIR, Raman and MAS NMR) provide the possibility of observing directly the interaction of adsorbed CFCs with zeolite adsorbents, and any subsequent reactions. Investigation of the adsorption and reaction of different CFCs on NaX- and NaY-FAU zeolites showed that the Raman band at 507 cm⁻¹ is related to dealumination of the zeolite during the surface reaction¹⁷. The type of the vacancy formed can be assigned to the band at 930 cm⁻¹ in the IR spectrum¹⁸. The ability of chlorine-containing molecules to promote dealumination of zeolites is well known¹⁹. The chemistry proposed for this process involves initial chlorination of the surface followed by elimination of AlCl₃²⁰.

Detailed FTIR (fourier transform infrared spectroscopy) and solid-state NMR studies of the interaction of CFCs with zeolites Y-FAU, mordenite and ZSM-5 showed that the ¹³C NMR spectrum of adsorbed CCl₂F₂ is shifted from that of the corresponding liquid²¹, and infrared spectra show shifting and broadening of the OH stretching bands of the zeolite, indicating an interaction of the CFC with both internal (acidic) OH groups and (non-acidic) silanol groups²². Spectroscopic studies provide evidence that CCl₂F₂ reacts more aggressively with zeolites at elevated temperatures. The extent and nature of reaction depends on the zeolite type and the exchanged cation. Signals in the ¹³C NMR spectrum of CCl₂F₂ adsorbed on NaY at room temperature were replaced on heating to 473 K by signals due to adsorbed phosgene (COCl₂) and CO₂. At higher temperatures (600 K), the ²⁹Si NMR spectrum showed that the zeolite structure was significantly degraded (about 50% amorphous phase formed). The ²⁷Al NMR spectrum revealed the formation of some octahedrally coordinated aluminium as well as significant loss of total signal intensity. The ²³Na NMR spectrum clearly showed the formation of NaCl, as well as possibly NaF. Zeolite HY-FAU was much more reactive towards CCl₂F₂ than NaY. At 500 K the reaction caused almost complete collapse of the zeolite, as judged from the ²⁹Si NMR spectrum. The ²⁷Al NMR spectrum showed the appearance of intense new features at about 0 ppm (octahedral aluminium) and 35 ppm. This third signal has been attributed to a deformed tetrahedral framework aluminium, or possibly pentacoordinated al-

(A) HY-FAU, (B) HM-MOR and (C) HZSM-5²⁶.

Fig. 1 IR Spectra of the Fresh (a) and Used (b) Samples

uminiun²³). Evidence for at least partial framework destruction in HY-FAU is also found in the infrared spectra of the framework stretching region showing the formation of a new band at 911 cm⁻¹ assigned to defect sites²⁴. Infrared spectra of the gas phase showed that the reaction products from CCl₂F₂ over HY were HCl, CO₂ and COCl₂²⁵. It is noteworthy that no fluorine-containing products were detected in the gas phase.

Zeolites MOR and MFI are more resistant to structural damage than the FAU structure, and this is also true in the reaction with CCl₂F₂²⁶. Structural changes were investigated by the KBr technique of IR spectroscopy. The spectra of various zeolites are shown in **Fig. 1**. The intensity of the new band around 930 cm⁻¹ was regarded as a measure for the concentration of defect sites¹⁸. The spectra show that this band appeared for each zeolite, with high intensity for HY-FAU and much lower intensity for HZSM-5-MFI. Furthermore, the band position also changed from 911 to 934 cm⁻¹ as indicated in **Fig. 1**. Comparison of the spectra shows a rather large shift in the frequencies of the structure-sensitive vibrations around 1030 cm⁻¹. This band shift is characteristic of the aluminium concentration in the framework. In this case, dealumination occurred during treatment of zeolites with CCl₂F₂. A higher shift indicates a greater degree of dealumination. The shift is the highest for HY-FAU zeolite (25 cm⁻¹), somewhat lower for HM-MOR (22 cm⁻¹) and even lower (10 cm⁻¹) for HZSM-5. This trend follows the thermal and hydrothermal stability order of zeolites, which correlates with the Si/Al ratio (2.5, 5 and 40, respectively).

After reaction at room temperature (a), at 473 K for 1 h (b), 4 h (c), 8 h (d) and 20 h (e)²⁶.

Fig. 2 ¹³C NMR Spectra of the Products of CFC-12 Decomposition over HZSM-5 Zeolite

¹³C NMR spectroscopy showed that decomposition of CCl₂F₂ adsorbed on HM-MOR and HZSM-5 occurs through similar pathways to that on HY-FAU, involving CCl₄ and COCl₂ as intermediates, with adsorbed CO₂ as the final carbon-containing product (**Fig. 2**). These molecules were also detected in the gas phase. ²⁷Al and ²⁹Si NMR spectra of the zeolites before and after treatment with CFC-12 at 600 K are plotted in **Fig. 3**. The ²⁹Si NMR spectrum of HY-FAU zeolite (spectrum b) is characteristic of an amorphous rather than a crystalline material. Structural unity was more deeply preserved for HM-MOR and HZSM-5-MFI, with only limited rearrangement in the coordination of silicon. In accordance with the ²⁹Si NMR spectra, the ²⁷Al NMR spectra also suggest amorphous material for HY-FAU, which is due to the lower Si/Al ratio in its framework. The presence of the octahedral aluminium species at ca. 0 ppm clearly shows that dealumination occurred in all three zeolites. ¹⁹F NMR spectroscopy revealed that fluorine was retained in the zeolite as AlF₃ (appearance of a ¹⁹F signal at -163.4 ppm besides the signal at -6.1 ppm due to the initially adsorbed CCl₂F₂)²⁴.

Besides the comparison of the reactivity of CCl₂F₂ over different zeolites, the reactivity of different CFCs over the same zeolites has also been compared²⁷. CFCs containing more than two fluorine atoms (CClF₃ and CF₄) underwent no reaction with NaY, HY or CuY. CCl₄ (CFC-10) and CCl₃F reacted similarly to CCl₂F₂, forming phosgene as intermediate and CO₂ as final

Before (a) and after (b) reaction with CFC-12 at 600 K²⁶⁾.

Fig. 3 ²⁷Al and ²⁹Si NMR Spectra of Zeolite HY-FAU (A), HM-MOR (B) and HZSM-5 (C)

product, and causing extensive structural damage to the zeolites. The phosgene intermediate is believed to be the key to the structural damage. Phosgene cannot be readily formed from CF₄ and CClF₃, so these CFCs do not react. The hydrogen-containing CFC CHClF₂ (HCFC-22) reacted slowly and CO was formed as a final product rather than CO₂.

The presence of the C-Cl bond is essential for the decomposition of CFCs, but two Cl atoms are required for the formation of the phosgene intermediate, which removes aluminium from the zeolite framework and causes the collapse of the crystal structure of the zeolite. Therefore, the zeolite should be regarded as a reaction partner and not as a catalyst. Such IR and NMR spectroscopic observations do provide considerable insight into how the CFC reactants interact with zeolite catalysts.

Investigation of the catalytic decomposition of CFCs over zeolites in the presence of water showed the reaction products were CO₂, HCl and HF²⁸⁾. The order of reactivity for different CFCs decreased from CCl₄ toward CF₄, as observed previously²⁷⁾. The differences in reactivity may account for the bond energy differences. The C-Cl bond energy increases from CCl₄ to CClF₃ (Table 1) suggesting that C-Cl bond cleavage is the rate determining step in the reaction. Simultaneously, the C-F bond energy also increases. The C-Cl bond energy is lower than that of the C-F bond in CFCs. Therefore, the chlorine atom can be removed during hydrogenation. Various zeolite-supported noble metal catalysts are active in the hydrodechlorination reactions

Table 1 Bond Energy of CFCs²⁹⁾

Compound	Bond energy [kJ·mol ⁻¹]	
	C-Cl	C-F
CCl ₄	305.9 ± 7.5	—
CCl ₃ F	305 ± 8	427 ± 9
CCl ₂ F ₂	346.0 ± 13.4	462.3 ± 10
CClF ₃	360.2 ± 3.3	490 ± 25
CF ₄	—	543 ± 4

of CFCs, but the catalysts are deactivated very fast.

Pd on activated carbon has technical as well as economic advantages as a catalyst for the selective hydrodehalogenation of CFC-12 (CCl₂F₂) into HFC-32 (CH₂F₂)³⁰⁾. Optimization of reaction conditions leads to high selectivity for HFC-32 (75%) combined with high conversion of CFC-12 (100%). The first step in the hydrogenolysis is the dissociative adsorption of CFC-12, which is followed by fast surface transformation into CF₂-carbene. This carbene can desorb through reaction with hydrogen to give HFC-32 or it can react further to give CH₂, which, finally, forms methane. Actually, small amounts of other hydrogenated intermediates such as CHClF₂ and CH₃F are also formed.

4. Adsorption and Transformation of Halons over Zeolites

The interaction of Halons (bromofluorocarbons) with zeolites has received much less attention than that of the corresponding CFCs, even though their conversion to less harmful alternatives which do not react with ozone is also very important. The Halons most frequently used as fire suppressants are Halon 1301 (CF₃Br) and Halon 1211 (CF₂ClBr)³¹⁾.

The C-Br bond strength in Halons is significantly lower than the corresponding C-Cl bond strength in CFCs. Average carbon-halogen single bond enthalpies are³²⁾: C-F = 485 kJ·mol⁻¹, C-Cl = 327 kJ·mol⁻¹, C-Br = 285 kJ·mol⁻¹ and C-I = 228 kJ·mol⁻¹. These data suggest that the catalytic chemistry already proposed for CFCs may also be applied to Halons.

Interesting experiments reacted CF₃Br over zeolite catalysts in the presence of CH₄ as a hydrogen source for hydrodehalogenation^{33),34)}. In the absence of catalyst, the homogeneous reaction of CF₃Br with CH₄ begins above 800 K and increases rapidly above 973 K. The products at lower temperatures are almost exclusively CHF₃ and CH₃Br. The reaction can be regarded as a simple hydrogen exchange between the two reactants. The initiation step is the homogeneous cleavage of a C-Br bond. The CF₃· radical then abstracts a hydrogen atom from CH₄, and the resulting CH₃· radical reacts with a bromine atom. At higher temperatures CH₃Br reacts further.

MFI zeolite catalysts reduce the temperature required for the reaction by about 150 K. Methane conversion does not, however, equal that of CF_3Br , suggesting that the reaction path is more complex than under homogeneous conditions. This is also evident from the product distribution obtained. Selectivity for CH_3Br consistently exceeds that for CHF_3 in contrast to the homogeneous reaction, in which CHF_3 has the highest yield. Other significant products detected in the catalyzed reaction, even at 873 K, are CH_2Br_2 , C_2F_6 , C_2H_4 and $\text{C}_2\text{F}_2\text{H}_2$. The catalytic transformation of other important Halons including 1211 (CF_2ClBr) has not yet been investigated over zeolites.

5. Hydrodechlorination over Zeolite Supported Catalysts

5.1. CCl_4

Investigation of the adsorption and reaction of CCl_4 on Pt-containing Y-FAU zeolite by IR spectroscopy³⁵⁾ adsorbed the reactant CCl_4 without hydrogen on the reduced noble metal-containing zeolite to obtain information about the surface species generated upon adsorption and in the reactions. The CCl_4 reacted with the oxygen-content of the zeolite framework and produces phosgene on the surface. The doublet at 1710 and 1800 cm^{-1} due to adsorbed phosgene is caused by the Fermi resonance between the fundamental vibration of $\text{C}=\text{O}$ bond and the overtone of the $\text{C}-\text{Cl}$ bond in adsorbed phosgene on zeolites free of Pt^{19),36)}.

CCl_4 decomposes via the consumption of O from the framework of the zeolites. All previous results have shown that the reactions take place on the zeolitic surface with the participation of the zeolite framework. From this follows that the transformation of CCl_4 over zeolite in the absence of hydrogen is a stoichiometric conversion, rather than catalytic, in which the decomposition of CCl_4 and the destruction of the zeolite framework occur simultaneously. Similar results were obtained for PtZSM-5 zeolite.

In the presence of hydrogen, the hydrodechlorination reaction over Pt-NaY-FAU zeolite forms methane and HCl as the main products in the gas phase, typical for the hydrodechlorination of carbon tetrachloride at higher temperature. As shown in **Fig. 4**, the characteristic absorptions of methane appeared in the C-H stretching region at 3050 cm^{-1} , and in the C-H deformation region at 1300 cm^{-1} . The bands centered at 2880 cm^{-1} are attributed to the characteristic vibration of HCl.

IR spectroscopy indicated that chloroform is an intermediate product of a consecutive transformation, because its characteristic absorption at 1210 cm^{-1} (due to C-H deformation vibration) passed through a maximum, indicating that Pt-supported zeolites are selective catalysts for the transformation of carbon tetrachloride to chloroform at lower temperatures (for example at

Fig. 4 Infrared Gas-phase Spectra of the Products of Carbon Tetrachloride Hydrodechlorination over Pt-NaY-FAU at 673 K (a), 573 K (b), 473 K (c) and 373 K (d)³⁵⁾

Fig. 5 IR Spectra of Pyridine Adsorption on Ion-exchanged Pt-NaY-FAU Zeolite, Evacuated at (a) RT, (b) 373 K, (c) 473 K, (d) 573 K and (e) 673 K¹²⁾

373 K). This finding is in good agreement with previous measurements over other supported Pt catalysts^{5),6)}.

In spite of the hydrogen atmosphere applied in these experiments, small amounts of the oxygen-containing intermediate product, phosgene ($\text{C}=\text{O}$ vibration at 1830 cm^{-1} and $\text{C}-\text{Cl}$ vibration at 850 cm^{-1}), were also detected on the ion-exchanged Pt-NaY-FAU sample with relatively high Brønsted acidity. The oxygen in phosgene originates from the zeolite framework.

Figure 5 shows the spectra of adsorbed pyridine on the ion-exchanged Pt-NaY-FAU zeolites reduced in hydrogen. The spectra all show high Brønsted acidity

Fig. 6 IR Spectra of Pyridine Adsorption on Impregnated Pt/NaY-FAU Zeolite, Evacuated at (a) RT, (b) 373 K, (c) 473 K, (d) 573 K and (e) 673 K¹²⁾

indicated by the absorption band of pyridinium ion at 1542 cm^{-1} . The region near 1450 cm^{-1} characteristic for Lewis acidity is more complex. The adsorbed pyridine at 1440 cm^{-1} shows weak Lewis acid sites because this peak disappeared on evacuation above 473 K.

This is due to pyridine probably adsorbed on Na^+ ions remained in the zeolite after ion exchange. Only a small amount of the true Lewis center was present as indicated by adsorbed pyridine at 1454 cm^{-1} .

The sample prepared by impregnation followed by treatment in hydrogen included a very small number of Brønsted acid sites as seen in **Fig. 6**. Lewis acid sites predominated in this sample. No phosgene was found on the impregnated Pt-NaY-FAU with no Brønsted acidity. The significant decrease in Brønsted acidity due to reduction with NaBH_4 resulted in similar observations for the PtZSM-5 zeolite. Formation of phosgene as a side reaction during hydrodechlorination was negligible without Brønsted acidity⁹⁾.

The situation is different over Pd-NaY-FAU zeolite³⁷⁾. IR spectra in **Fig. 7** reveal that this catalyst was less active in the hydrodechlorination of carbon tetrachloride than Pt-NaY-FAU. Products are visible in the spectra taken above 473 K. There was no chloroform among the reaction products, but a small amount of carbon monoxide was detected. The other difference is the high amount of ethane besides methane in the final product. Ethane is indicated by a broad band at 3000 cm^{-1} and a smaller one near 1500 cm^{-1} due to the C-H stretching and deformation vibrations of ethane as in **Fig. 7e**.

Adsorption of halogenated hydrocarbons on the metal

Fig. 7 IR Gas-phase Spectra of the Products of Hydrodechlorinated CCl_4 on Pd-NaY-FAU Zeolite, Evacuated at (a) RT, (b) 373 K, (c) 473 K, (d) 573 K and (e) 673 K³⁷⁾

surfaces causes breaking of a C-Cl bond. The rate and extent of this reaction depends on the nature of the metal cluster. Recent discussion of the hydrodehalogenation of some chloro(fluoro)carbons over alumina-supported Pt and Pd catalysts concluded that Pt was "more noble" than Pd and, therefore, both the reactants and the intermediates were less strongly bonded to the platinum surface⁴⁾.

After bond dissociation, the adsorption strength of the fragments, or in other words the desorption ability of chlorine atoms, influences further reactions. The two main reaction paths are hydrogen insertion followed by desorption and further cleavage of the C-Cl bonds in the surface fragments, finally resulting in the release of hydrocarbons like methane and ethane (or ethylene). Both hydrogen insertion and hydrogenation take place on noble metal surfaces. As the bond strength between fragments of carbon tetrachloride is stronger over Pd centers than Pt sites, the probability of hydrogen insertion into the same fragment is higher on Pd than on Pt. Consequently, the main product is methane over Pt-containing material, and ethane over Pd. Our spectroscopic findings support this reasoning.

5.2. C_2 Chlorocarbons

Hydrodechlorination of trichloroethene and 1,1,2-trichloroethane was compared over Pt- and Pd-containing zeolites under the same reaction conditions applied for carbon tetrachloride³⁸⁾. The only reaction products in the gas phase were ethane and HCl over Pt- and the Pd-containing zeolite catalysts. The reactants were less strongly bonded to Pt than to Pd resulting in higher activity. The selectivity was similar under the experimental conditions applied.

5.3. Chlorobenzenes

Platinum loaded HBEA zeolite has been used for the gas-phase hydrodechlorination of chlorobenzene³⁹⁾. The major reaction products are benzene and cyclohexane along with HCl. Over the zeolite supported

catalyst, some isomerization of cyclohexane to methylcyclopentane is also observed. The zeolite-supported catalyst deactivates with time on stream, which is attributed to the presence of Brønsted acid sites. These acid sites promote the oligomerization of cyclohexene intermediate species leading to coke formation. The performance of Pt-alumina was much better, suggesting that in this case there is no particular advantage of using a zeolite support. Similar conclusions may be drawn from the comparison the performance of Ni/SiO₂ and Ni-Y catalysts for the gas-phase hydrodechlorination of pentachlorophenol⁴⁰.

5.4. Ground-water Treatment

A particular problem is dealing with halogenated hydrocarbons in contaminated ground water using catalytic hydrodehalogenation. Palladium based catalysts can readily hydrogenate contaminants such as trichloroethene and perchloroethene even at room temperature yielding ethane and HCl. Zeolite supported palladium catalysts have been developed, which can be effectively used in the treatment of real ground water samples^{41,42}.

Palladium catalysts supported on different zeolites and mesoporous MCM-41 with different Si/Al ratios were tested in the hydrodechlorination of 1,2-dichlorobenzene in water at room temperature. The activity for 1,2-dichlorobenzene conversion to benzene and HCl increased with increasing pore size of the zeolite. The highest activity was shown by the Pd-MCM-41 catalysts, with pore diameters of more than 2.5 nm.

The remarkable poison resistance of the Pd-Y catalyst was attributed to the hydrophobicity of the support, based on the idea that 1,2-dichlorobenzene can penetrate into the zeolite pores to be hydrogenated at the palladium sites, whereas aqueous sulphite cannot penetrate and poisons only those palladium sites on the external surface of the zeolite⁴². This work demonstrates the potential of engineering the pore size and hydrophobicity of zeolite supports to obtain hydrodehalogenation catalysts that may be used under realistic industrial waste treatment conditions³¹.

6. Conclusions

Adsorption and transformations of various chlorofluorocarbons (CFCs), bromofluorocarbons (Halon) and chlorinated hydrocarbons over zeolites were reviewed. The order of reactivity for different CFCs decreases from CCl₄ toward CF₄. The differences in reactivity may be related to the bond energy differences.

IR and NMR studies proved that the fluorine content of CFCs is retained in the zeolite as AlF₃ and dealumination occurs. As a consequence, the crystal structure of the zeolite collapses and the zeolite should be therefore regarded as a reaction partner and not as a catalyst⁴³. The resistance of the zeolites increases with the Si/Al ratio, as MOR and MFI are more resistant to

structural damage than the FAU structure in the reaction with CCl₂F₂.

The interaction of Halons with zeolites has received much less attention than that of the corresponding CFCs, but CF₃Br was hydrodehalogenated in the presence of methane as hydrogen source on MFI zeolite catalyst to CH₃Br and CHF₃.

Hydrodechlorination of carbon tetrachloride was applied as a model reaction for testing Pt- and Pd-containing zeolites. The Pt-containing zeolite catalyst was more active in this reaction than the Pd-containing catalyst, and methane and HCl as the main products were formed, with chloroform as intermediate product. No chloroform but high amounts of ethane as final product besides methane were formed on Pd-containing zeolite. The bond strength between fragments of carbon tetrachloride is stronger over Pd centers than on Pt sites, so the probability of hydrogen insertion into the same fragment is higher on Pd than on Pt. Consequently, the main product is methane on Pt-containing material, and ethane on Pd.

When noble metal-containing zeolites are prepared by ion exchange and reduced in hydrogen Brønsted acid sites are formed as well as the metal centers. The transformation mechanisms of the chlorinated hydrocarbons over this type of zeolite are very complex. When the adsorption takes place on the Brønsted acid sites, decomposition of the chlorinated molecules may take place and the product of this reaction is oxygen-containing compound (phosgene). The presence of oxygenate indicates the partial decomposition of the zeolite framework by the formation of lattice vacancies with increasing concentrations. This type of reaction should be considered as a stoichiometric transformation and not a catalytic conversion of chlorinated hydrocarbon. The formation of Brønsted acid sites can be avoided using reducing agents other than hydrogen, *e.g.*, NaBH₄, or other preparation method than ion exchange *e.g.*, impregnation with metal salts.

The results of IR and NMR spectroscopy proved that the acid resistance of the zeolites in the hydrodechlorination reaction increases with the Si/Al ratio. For the preparation of high-performance zeolite-supported catalyst zeolite with high Si/Al ratio, for example, ZSM-5 is suggested.

The use of hydrophobic zeolite or zeolite-like mesoporous silicate (*e.g.* MCM-41) supported catalysts to effectively treat chlorocarbon contaminated waste water streams offers opportunities worthy of further scrutiny.

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要 旨

ゼオライト担持触媒による水素化脱塩素
—反応機構の解明—

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大気中に放出される塩素化合物は成層圏のオゾン層を破壊する原因となっている。塩素化合物の処理法として、酸化して環境に優しい化合物に変換する方法と水素化脱塩素して有用な化合物に変換する方法が主流となっている。

本論文では、触媒上での水素化脱塩素の反応機構を解明するため、ゼオライトおよび貴金属含有ゼオライト触媒上でのハロゲン化合物の挙動を分光学的手法（IR, NMR など）により分析した。

NMR の検討から、反応温度の上昇に伴い、クロロフルオロカーボンのゼオライトに対する反応性が増すことがわかった。水素化脱塩素の反応性は、ゼオライトの種類やイオン交換され

たカチオン種に依存した。気相の IR 分析の結果、 CCl_2F_2 の水素化脱塩素では、 HCl 、 CO_2 および COCl_2 が反応生成物として検出された。ホスゲン中間体の生成がゼオライト骨格を破壊する主因であると考えられる。

四塩化炭素の水素化脱塩素では、白金含有ゼオライト触媒はパラジウム含有ゼオライト触媒に比べて活性が高く、主生成物であるメタンおよび塩化水素以外にクロロホルムが中間体として生成していた。

種々の塩素含有化合物（フッ素を含むあるいは含まない C1 、 C2 化合物）の異なる金属を含有する種々のタイプのゼオライトによる水素化脱塩素の活性、選択性についてまとめた。

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