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Journal of Catalysis 215 (2003) 234–244

JOURNAL OF
CATALYSIS

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Oxidation of chlorinated hydrocarbons over Pt zeolite catalysts 1-mechanism of dichloromethane transformation over PtNaY catalysts

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Received 1 September 2002; revised 4 December 2002; accepted 4 December 2002

Abstract

The catalytic oxidation of dichloromethane (DCM, 1000 ppm) in wet air was carried out in a fixed bed reactor over NaY, pure, exchanged with 0.5 wt% Pt or added with 0.4 wt% $PtSiO_2$. At low temperatures ($\leqslant 250\ ^\circ C$) DCM is selectively hydrolyzed into $2/1$ molar mixture of HCl and formaldehyde; at higher temperatures with Pt catalysts, DCM hydrolysis is followed by formaldehyde oxidation into CO_2 and water, which suggests a bifunctional scheme. DCM transformation was investigated over pure NaY, the zeolite samples being characterized after reaction by adsorption of nitrogen, of pyridine followed by IR spectroscopy, and of DCM followed by microcalorimetry. During the first 15 min of reaction, a significant decrease in conversion could be observed as well as large changes in the NaY properties: disappearance of the strongest sites for DCM adsorption, creation of acidic bridging OH groups, etc., suggesting a stoichiometric reaction of DCM with NaY. Afterward, the process became catalytic with no more change in DCM conversion and in the physicochemical properties of the zeolite. A mechanism of DCM hydrolysis is proposed involving as intermediates chloromethoxy, hydroxymethoxy, and NaCl species as well as the OH groups created on the NaY zeolite.

Keywords: Total oxidation; Chlorinated hydrocarbons; Dichloromethane; Hydrolysis; PtNaY catalysts; Deactivation

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1. Introduction

Chlorinated volatile organic compounds (ClVOCs) are found in many gas emissions. Thus, about 1.5 million tons of chlorinated compounds per year can be released in the atmosphere [1], generated either in chemical plants (e.g., vinylchloride production plants [2]) or in dry cleaning and degreasing processes [3,4]. Catalytic combustion is one of the most promising technologies for the elimination of ClVOCs; the objective is to transform completely these compounds into environmentally harmless substances at low temperatures and short residence times. Of course, no toxic byproducts (carbon monoxide, chlorine, phosgene, polychlorinated compounds) must be formed even in traces. Metal oxides [5–14], either single (e.g., chromium oxide) or mixed (e.g., perovskites) and supported noble metals [5,15–26] are generally proposed for ClVOCs oxidation. For both types of catalysts, deactivation is one of the main problems to be solved [5].

There are also various studies of the oxidation of chlorinated hydrocarbons over zeolites [27–37] and mesoporous molecular sieves [38]. Acidic zeolites: HFAU, HMOR, HMFI, such as those loaded with Co or Cr, were shown to be active but not very selective, forming CO, Cl_2, and chlorinated byproducts, and not very stable. However, it has been recently shown that platinum improved significantly the catalytic properties of a HFAU sample, allowing in the presence of water, a complete and stable transformation of dichloromethane into the desired products: CO_2, H_2O, and HCl [37]. Both the protonic sites and the platinum sites were shown to participate in this transformation.

In this paper, dichloromethane (DCM) transformation was investigated over PtNaY catalysts. These catalysts were found to be more active than PtHFAU samples [37]. But again, DCM conversion occurred through a bifunctional process, involving successively DCM hydrolysis over NaY into formaldehyde and hydrochloric acid then oxidation of formaldehyde over Pt sites into CO_2 and water. A kinetic study of DCM hydrolysis was carried out on pure NaY. Proposals are advanced to explain the hydrolysis mechanism as well as the significant changes in the physicochemical

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doi:10.1016/S0021-9517(02)00189-6

properties of NaY, which occurred during the first minutes of reaction.

2. Experimental

2.1. Catalyst preparation

The NaY sample (Si/Al = 2.45) was supplied by Union Carbide. The 0.5 wt% PtNaY sample supplied by IRMA, Ploemeur was prepared though the following steps: exchange of NaY with $Pt(NH_3)_4{}^{2+}$ in competition with $NH_4{}^+$, calcination under dry air flow at 450 °C for 2 h. The 0.4 wt% $PtSiO_2$ sample results from impregnation of SiO_2 with $[Pt(NH_3)_2(NO_2)_2]$, then calcination under air at 450 °C for 4 h. The dispersion of Pt was determined by CO adsorption followed by IR spectroscopy [39].

2.2. Catalyst characterization

Elemental analysis of the samples was carried out by the Centre d'Analyse CNRS of Vernaison. Nitrogen adsorption measurements were performed at −196 °C with the gas adsorption system ASAP 2000 (Micromeritics).

IR spectra were recorded with a Nicolet Magna IR 550 spectrometer using thin wafers of 5–15 mg cm^{-2} activated in situ in the IR cell in vacuum (10^{-3}) at 200 °C for 2 h. Pyridine was adsorbed on the sample at 150 °C. The IR spectra were recorded at room temperature after activation and after pyridine thermodesorption in vacuum (10^{-3} Pa) for 1 h at 150 °C. The concentrations of Brønsted and Lewis sites able to retain pyridine adsorbed at 150 °C were determined from the absorbance surface of the bands at 1545 and 1450 cm^{-1} respectively using the extinction coefficients previously determined [40].

A Setaram DSC 111 calorimeter equipped with a volumetric vacuum line was used for microcalorimetric measurements. Each sample (100 mg) was pretreated overnight at 200 °C under vacuum (10^{-3} Pa). Adsorption was carried out at 25 °C by admitting successive doses of dichloromethane and recording the thermal effect.

2.3. Dichloromethane transformation

DCM transformation was carried out at constant temperature in a fixed bed reactor containing 140 mg of the NaY component of the catalyst. A fresh catalyst sample was used for each experiment. The standard feed (with 2.7 mol% water) is obtained from the mixture of reconstituted air (nitrogen + oxygen only) containing 3000 ppm of DCM and of reconstituted air having passed in a saturator containing water at 25 °C. The space velocity (volume of feed introduced per volume of the catalyst bed and per hour) is always fixed to 20,000 h^{-1} with respect to the NaY component. The effluent gases were analyzed online by using two GC apparatus; the first apparatus was equipped with two columns and two detectors: a CPSil 5 capillary column linked to a FID detector for the quantitative analysis of organic reactant and products, a Porapak Q column linked to a TCD detector for the quantitative determination of CO_2; the second apparatus, equipped with a 13X molecular sieve column and a TCD detector, was used to determine the production of CO. Hydrochloric acid was recovered in water and its amount estimated by pH measurement. Mass spectrometry (MS) and specific Dräger tubes were used for detecting the eventual production of Cl_2 and of phosgene (never observed in this work). Furthermore, GC-MS analysis allowed us to confirm the formation of formaldehyde.

3. Results

3.1. Dichloromethane transformation on NaY, PtNaY, and $PtSiO_2/NaY$ samples

Dichloromethane transformation was carried out over various catalyst samples: NaY, intimate mixtures of 0.4 $PtSiO_2$ (platinum dispersion of 18%) and NaY, a 0.5PtNaY catalyst (dispersion of 15%) prepared by exchange of NaY with $Pt(NH_3)_4Cl_2$ in the presence of $NH_4{}^+$ as competition ions. There are important differences between the physicochemical characteristics of NaY and 0.5PtNaY. The introduction of Pt causes, as expected from the exchange conditions, the elimination of Na cations (38%), hence the development of acidic OH groups. Pyridine adsorption followed by IR spectroscopy shows that this sample contains 66 µmol g^{-1} of protonic sites able to retain pyridine adsorbed at 150 °C.

With all samples except 0.5PtNaY, there is, in the presence of water (standard feed), a very fast initial decrease in conversion followed by a plateau (Fig. 1a). Thus, at 300 °C with NaY, DCM conversion which is equal to 80% at 5 min of reaction is afterward practically constant: 61% after 15 min and 58% after 3 days; the adding of $PtSiO_2$ to NaY causes an initial increase in activity but at the plateau, DCM conversion is close to that found with pure NaY (Figs. 1a and 1b). At this temperature, no conversion of DCM can be observed over pure $PtSiO_2$. With 0.5PtNaY, the conversion is always constant but lower than with the other samples (44%).

With all samples, CO_2, HCl, and formaldehyde appear in the reaction products in relative amounts depending on temperature and on time on stream. CO is observed with NaY only. Furthermore, we have checked through MS analysis that neither organic products other than formaldehyde nor Cl_2 and $COCl_2$ (also not detected with Dräger tubes) were in the effluents.

At 300 °C, there is initially formation of formaldehyde, HCl, and CO_2 (and H_2O) with all the catalysts even with NaY. With this latter catalyst, CO_2 formation decreases rapidly becoming zero at the activity plateau. With the $PtSiO_2/NaY$ mixtures, this formation becomes roughly pro-

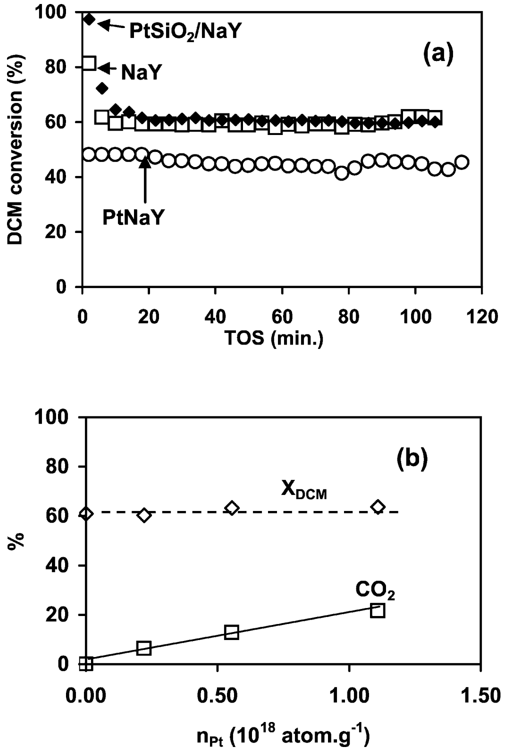


Fig. 1. Transformation of dichloromethane (DCM) at 300 °C over various catalysts (a) conversion of DCM versus time on stream, (TOS) on 140 mg of NaY pure or added with 140 mg of $PtSiO_2$ and on 140 mg of 0.5PtNaY; (b) conversion of DCM (X_{DCM}) and yield in CO_2 over stabilized mixtures of NaY (140 mg) and $PtSiO_2$ (0, 30, 70, and 140 mg) versus n_{Pt} the concentration of accessible Pt atoms per gram of NaY.

portional to the amount of $PtSiO_2$ added to NaY (Fig. 1b). With 0.5PtNaY, the conversion of DCM into CO_2 is independent on time on stream and equal to 30%. This conversion is 1.4 times higher than on the $1/1$ $PtSiO_2/NaY$ mixture, which has 1.35 times less accessible Pt atoms.

Fig. 2 shows the effect of temperature on the yields in formaldehyde, CO, and CO_2 obtained after 2 h of reaction on NaY, 0.5PtNaY and on the equimassic $PtSiO_2/NaY$ mixture. With all samples, formaldehyde (+ HCl) is the only reaction product at low temperatures ($\leqslant$ 300 °C with NaY, $\leqslant$ 260 °C with the bifunctional catalysts). With NaY (Fig. 2a), the yield in formaldehyde passes through a maximum (75%) at 340 °C; CO appears at this temperature and CO_2 at 420 °C, the yields in these latter products increasing with temperature at the expense of the yield in formaldehyde. Therefore the following successive scheme can be proposed for DCM transformation:

$$CH_2Cl_2 \overset{1}{\underset{-2HCl}{\overset{+H_2O}{\rightarrow}}} HCHO \overset{2}{\underset{+1/2O_2}{\rightarrow}} CO + H_2O \overset{3}{\underset{+1/2O_2}{\rightarrow}} CO_2 + H_2O. \tag{1}$$

With the bifunctional catalysts: 0.5PtNaY (Fig. 2b) and $PtSiO_2/NaY$ mixtures (e.g., the equimassic mixture (Fig. 2c)), there is also a maximum in the yield in formaldehyde, this product disappearing completely at the profit of

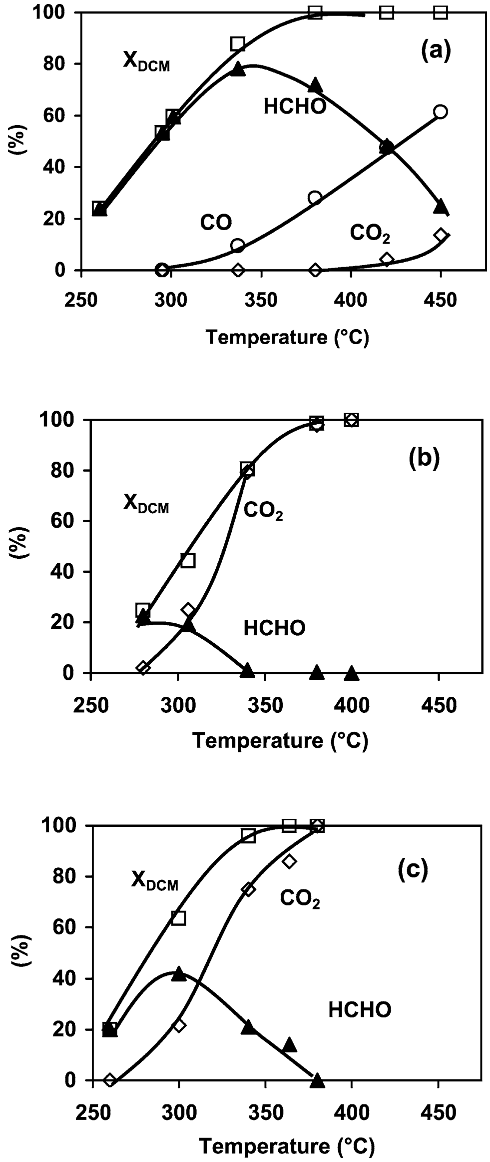


Fig. 2. Influence of reaction temperature on the conversion of dichloromethane (X_{DCM}) and on the yields in CO, CO_2, and formaldehyde (HCHO) after 2 h of reaction; (a) NaY (140 mg); (b) 0.5PtNaY (140 mg); and (c) $PtSiO_2/NaY$ mixture (140 + 140 mg).

CO_2; no CO can be observed in the reaction products. Therefore, DCM transformation appears to occur through a two-step successive scheme:

$$CH_2Cl_2 \overset{1}{\underset{-2HCl}{\overset{+H_2O}{\rightarrow}}} HCHO \overset{4}{\underset{+O_2}{\rightarrow}} CO_2 + H_2O. \tag{2}$$

Step 1 of reactions (1) and (2) implies water as a reactant, two molecules of hydrochloric acid being formed per molecule of formaldehyde. A molar HCl/formaldehyde (+ CO + CO_2) ratio of 2 was furthermore observed with all the stabilized catalysts and this, whatever the reaction temperature. However, this is not the case during the initial period of deactivation (ratio lower than 2). Step 2 (reaction (1)) occurs probably through a two-step successive scheme involving formic acid as formal (and highly reactive) intermediate:

$$\mathrm{HCHO} \underset{+1/2\mathrm{O}_2}{\rightarrow} \mathrm{HCOOH} \rightarrow \mathrm{CO} + \mathrm{H_2O}. \tag{3}$$

With NaY, CO_2 is formed above 420 °C by oxidation of CO (step 3, reaction (1)), most likely on Na cations. Indeed oxidative properties of Na cations have been previously demonstrated [41–43]. With the bifunctional catalysts, CO_2 appears at low temperatures due to the high oxidative activity of Pt sites.

The very close values of DCM conversion found at 300 °C with NaY, pure or added with various amounts of $PtSiO_2$ (stabilized catalysts) show that step 1 of reactions (1) and (2) is the determining step of DCM transformation. Therefore, the characteristics of the NaY part of the bifunctional catalyst determine the rate of this transformation. This could explain the lower activity of the 0.5PtNaY catalyst. Indeed, in this catalyst, part of the Na cations of NaY were exchanged during the introduction of Pt with creation of acidic hydroxyl groups and protonic Y zeolites were found to be less active than NaY: thus, DCM conversion under standard conditions decreased from 60% on NaY to 8% after a protonic exchange of 60% [44]. To assess more quantitatively this proposal, a NaHY sample was prepared by conventional exchange (exchange with NH_4NO_3 solution then calcination at 500 °C under dry air flow) at approximately 38% of NaY in order to obtain the same exchange level that PtNaY. The conversion of DCM on this NaHY sample (protonic exchange of 33%, protonic acidity close to that of PtNaY: 58 instead of 66 µmol protonic sites g^{-1}) was found to be close to that found on 0.5PtNaY: 42% at 300 °C instead of 44% demonstrating that the lowest activity of 0.5PtNaY was due to the partial exchange of Na during Pt introduction. Another important remark is that, like with PtNaY, no initial deactivation of NaHY can be observed.

3.2. DCM transformation over NaY—influence of the operating conditions

A kinetic study of DCM transformation was carried out over NaY at 300 °C, the temperature at which formaldehyde and HCl are the only reaction products (Fig. 2a). The conversion is independent on DCM concentration in the feed mixture (Fig. 3a); i.e., the rate of DCM transformation is proportional to DCM concentration (order equal to 1). This order is confirmed by the effect of contact time: $-\ln(1-X)$ is proportional to the contact time (Fig. 3b). The apparent activation energy estimated between 250 and 300 °C was found to be equal to 20 ± 2 kcal mol^{-1}. Identical results were obtained under standard conditions and when air was substituted by nitrogen, indicating that, as expected from step 1 in reactions (1) or (2), oxygen does not intervene in formaldehyde production.

When the amount of water is much greater than that necessary for step 1 (0.1 mol% at total conversion), no effect of the percentage of water can be observed both on catalyst stability and on DCM conversion (Fig. 4a), i.e., reaction order with respect to water equal to 0. However, in the absence of water, there is no appearance of products in the effluents, except a small amount of HCl due most likely to the presence of water traces in air (≈ estimated to 5 ppmv). The initial DCM conversion is high, close to that found in presence of water but deactivation is very fast (Fig. 4b). Furthermore, despite the low conversion of DCM after 10 min of reaction, the amount of C deposited on NaY is slightly greater than that in the presence of water and the amount of Cl is twice greater. A semiquantitative balance confirms that most of the products of DCM conversion remain blocked on the catalyst. Substituting after 2 h reaction the feed without water by the standard feed causes an increase in conversion (from 6% to 30%) and a catalyst stabilization (Fig. 4c). This conversion is, however, lower than in the experiments carried out directly in the presence of water (30% instead of 60%). Furthermore, after this experiment in two stages (without then with water) the percentage of Cl on the catalyst is equal to 1.05 wt% instead of 2.75 wt% after the experiment without water. This elimination of Cl from the catalyst can be explained by an overproduction of HCl observed during the second stage of the experiment.

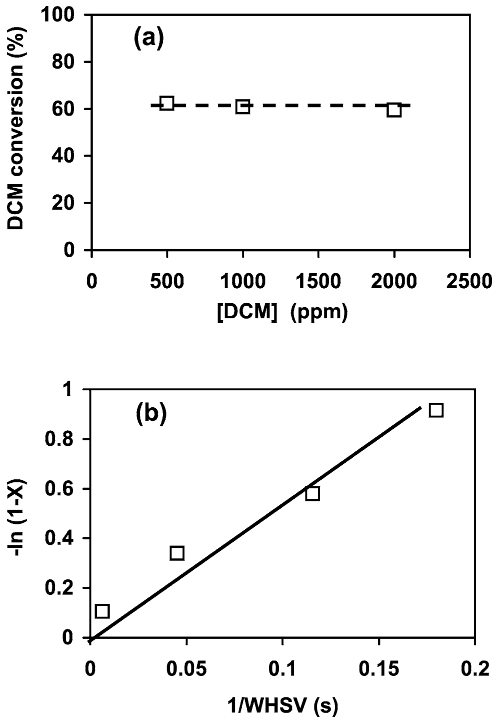


Fig. 3. (a) Influence of the concentration of dichloromethane in the feed on DCM conversion; (b) plot of the first-order equation: $-\ln(1-X)$ versus contact time taken here as the reverse of volume space velocity (1/WHSV).

3.3. Effect of dichloromethane transformation on the physicochemical characteristics of the catalyst

The NaY sample was characterized after DCM transformation at 300 °C with the standard feed (effect of time on

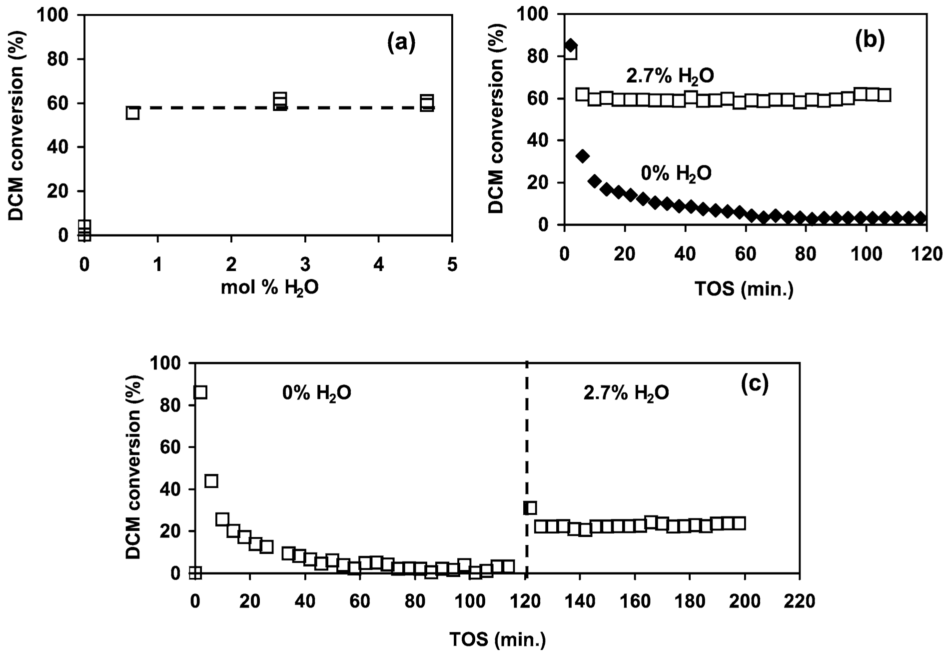


Fig. 4. Influence of water on the transformation of dichloromethane over NaY at 300 °C; (a) DCM conversion after 2 h of reaction versus the concentration of water in the feed; (b) comparison of the effect of time on stream on DCM conversion in presence and in absence of water; (c) DCM conversion in the absence then in the presence of water on the same sample versus time on stream.

stream), with the feed without water after 2 h of reaction and after the experiment in two stages without water for 2 h then with water for the same time.

Elemental analysis (Table 1) shows an elimination of Na from all the samples as well as a deposit of carbonaceous (wt% C) and chlorinated (wt% Cl) compounds. It should be underscored that the values of wt% C are too weak to be considered for a quantitative analysis. However, the results suggest that carbon deposit occurs mainly during the first minutes of reaction. This is also the case for Na elimination: 13% after 2 h, only 20% after 72 h in the presence of water. Water has practically no effect on the degree of Na elimination (Table 1).

Nitrogen adsorption was carried out over samples A, D, and F. With the three samples, the isotherm is of type I in the classification of Brunauer and Emmet [45]. The total pore volume and the micropore volumes were similar among the three samples (0.32–0.34 $cm^3\,g^{-1}$ and 0.30–0.32 $cm^3\,g^{-1}$, respectively). Therefore, there is no effect of DCM transformation (even in the absence of water) on the porosity.

Table 1
Influence of DCM transformation on the physicochemical properties of NaY

	A	B	C	D	E	F	G
Reaction time (h)	0	0.09	0.25	2	72	2	2 + 2
Water	–	yes	yes	yes	yes	no	no–yes
wt% C	–	0.15	/	0.21	0.11	0.25	0.17
wt% Na	10.5	/	/	9.15	8.4	8.9	9.35
wt% Cl	0	0.7	/	1.4	1.1	2.75	1.05
$A_{3744\,cm^{-1}}$	0.26	0.39	0.34	0.34	0.35	0.19	0.41
$A_{3644\,cm^{-1}}$	0	0.19	0.59	0.92	0.25	0.57	0.09
$A_{3617\,cm^{-1}}$	0	0	0	0	0.04	0.48	0.32
$n_{B(\mu mol\,g^{-1})}$	0	72	103	107	64	308	90
$n_{L(\mu mol\,g^{-1})}$	0	0	0	0	0	14	4

A, integrated absorbance, n_B, n_L concentrations of Brønsted and Lewis acid sites.

DCM transformation causes the appearance of hydroxyl bands in the I.R. spectra (Fig. 5a). Whereas NaY presents only a small hydroxyl band at 3744 cm^{-1} (silanol groups), another hydroxyl band at 3649 cm^{-1}, corresponding to bridging OH groups (SiOHAl) located in supercages [46], appears after reaction. Whereas this band increases significantly during the first 2 h of reaction, it becomes smaller at long time on stream as shown for sample E (Fig. 5); in the spectrum of this sample there are two additional bands, the first band at 3694 cm^{-1}, which could correspond to OH groups of extra framework Al species (EFAL), the second band very large at low frequency corresponding most likely to bridging hydroxyls located in hexagonal prisms. With NaY used in the absence of water (sample F, Fig. 6a), the spectrum is more complex comprising five bands corresponding to silanol groups (3744 cm^{-1}), EFAL species (3694 cm^{-1}), bridging OH groups located in supercages in interaction (3617 cm^{-1}) or not (3644 cm^{-1}) with EFAL species and bridging OH groups located in hexagonal prisms (3562 cm^{-1}). When sample F is used in the presence of water (sample G), there is an apparent increase of the silanol band and a decrease of the bands at 3644 and 3562 cm^{-1}.

Pyridine adsorption was carried out at 150 °C; Figs. 5b and 6b present the OH groups which were not affected by pyridine (nonacidic or/and nonaccessible by pyridine).

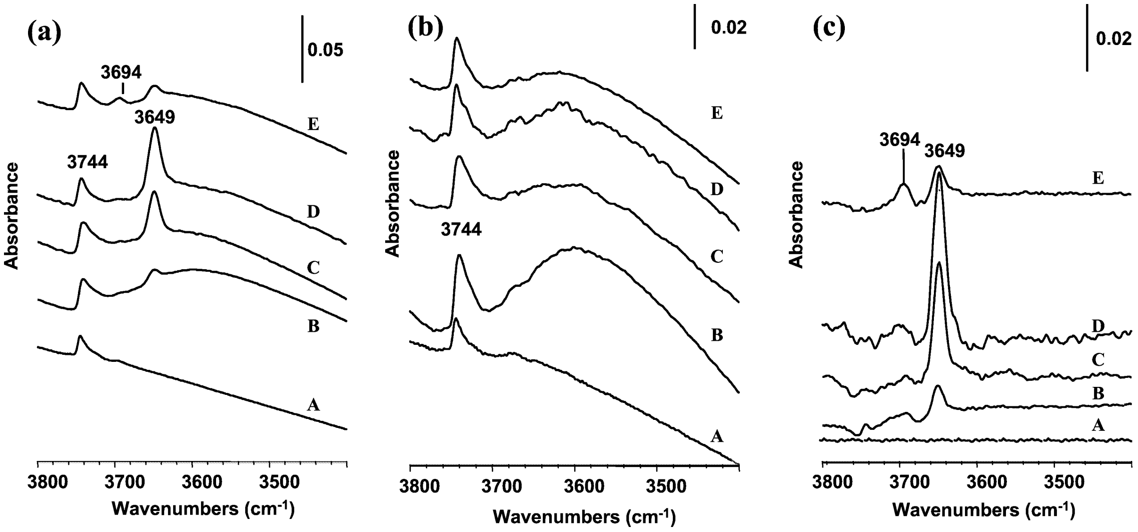


Fig. 5. IR spectra in the hydroxyl region for NaY samples used in DCM conversion with standard feed for different times on stream: (A) TOS = 0; (B) 0.09 h; (C) 0.25 h; (D) 2 h; (E) 72 h. (a) after the activation treatment, (b) after pyridine adsorption then desorption at 150 °C, (c) difference spectra a–b.

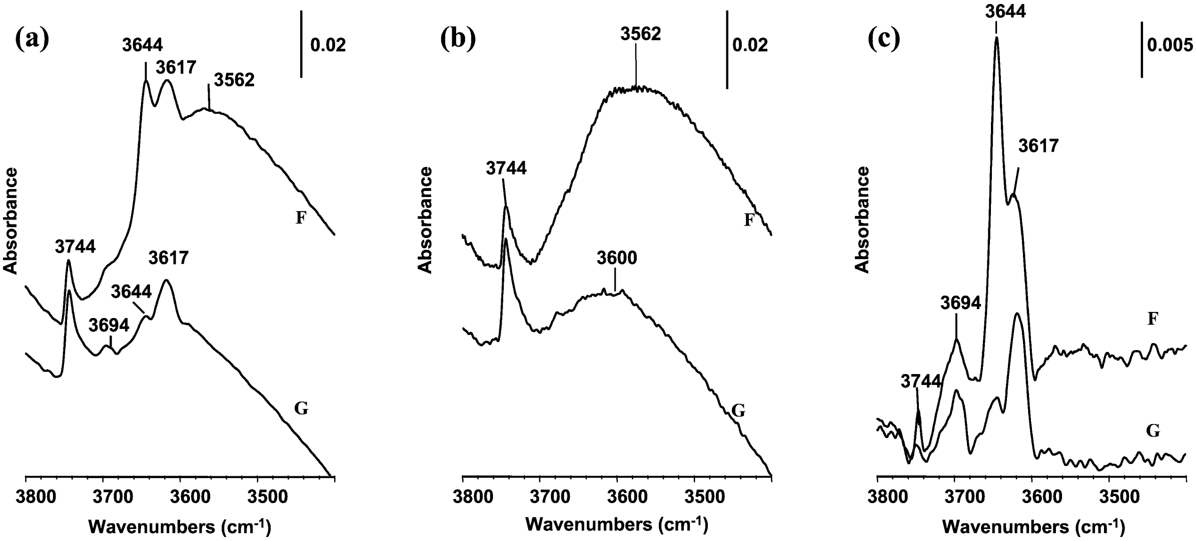


Fig. 6. IR spectra in the hydroxyl region of the NaY sample used in DCM conversion for 2 h in the absence of water (sample F) then for 2 h in the presence of water (sample G). (a) After the activation treatment, (b) after pyridine adsorption then desorption at 150 °C, (c) difference spectra a–b.

Figs. 5c and 6c present those which disappear by pyridine adsorption (acidic sites). With all the samples, pyridine adsorption had no effect on the silanol band. It had also no effect on the large band observed at low frequency with sample F (Fig. 6). The corresponding OH groups are therefore nonacidic or nonaccessible by pyridine. On the other hand, the bands at 3644–3649 cm^{-1} and at 3617 cm^{-1} which correspond to bridging OH groups of the supercages disappear, which confirms their acidity and their accessibility by pyridine molecules. With all the samples, a large band appears at approximately 3600 cm^{-1}. This band can be tentatively ascribed to the shift of the band at 3644 cm^{-1} toward low frequencies owing to hydrogen bond with pyridine. Indeed the protonic sites created by a limited exchange of NaFAU zeolites are very weak [46], hence often unable to protonate pyridine molecules.

The absorbances of the OH bands after activation and of the acidic OH bands were estimated from the spectra in Figs. 5, 6a, and 6c. Although the values (and especially those drawn from Figs. 5a and 6 for which deconvolution of the bands is impossible) lack precision, they allow a semi-quantitative analysis of the effect of operating conditions (Table 1). Reaction with standard feed causes from the first minutes of reaction a slight increase of the silanol band at 3744 cm^{-1} and the appearance of the band at 3649 cm^{-1} corresponding to acidic OH groups. After 5 min of reaction, the intensity of the silanol band remains constant; the intensity of the 3644 cm^{-1} band increases rapidly with time on stream then becomes quasi constant after 15 min reaction. At longer times, a band appears at 3617 cm^{-1} corresponding to acidic OH groups (Table 1). Reaction in the absence of water (sample F) has a slight negative effect in the intensity of the silanol band but causes the appearance of intense bands at 3644 and 3617 cm^{-1} (acidic OH groups) and at 3562 cm^{-1} (nonaccessible OH groups). DCM transformation (standard feed) on sample F causes an increase in the silanol groups, a small decrease of the band at 3617 cm^{-1}, a very significant decrease of the band at 3644 cm^{-1} and the disappearance of the band at 3562 cm^{-1} (sample G, Table 1 and Fig. 6).

Reaction with DCM causes also the appearance of various other IR bands essentially in the 1300–1800 cm^{-1} region, which correspond to species strongly retained on the catalyst. Part of these bands can also be found after formaldehyde adsorption on NaY [47]: bands at 1725, 1643, 1500, 1415 cm^{-1}; the small bands at 1385 cm^{-1} and 1641 cm^{-1} could correspond to formate ions.

The concentration of protonic sites was estimated from the integrated intensity of the pyridinium ion band at 1545 cm^{-1} by using as value of the extinction coefficient that (1.8 μmol^{-1} cm) previously determined by Lavalley and coworkers [40]. Table 1 shows that during the first 5 min of reaction with the standard feed, there is appearance of 72 $\mu mol\,g^{-1}$ of protonic sites in the zeolite. Afterward, the concentration of protonic sites increases slowly with time on stream. With the four samples B, C, D, and E, no band corresponding to pyridine coordinated to Lewis acid sites (1445 cm^{-1}) can be observed: there is no creation of Lewis acid sites during the reaction. For sample F that used 2 h in the absence of water, the concentration of protonic sites is very high, three times that of sample D that used 2 h in the presence of water and a small band corresponding to pyridine coordinated to Lewis sites can be observed. The use of F for DCM transformation in the presence of water causes a large decrease in acidity; the acidity of the obtained sample (G) becomes close to that of sample D (Table 1).

Dichloromethane adsorption on samples A, D, and F was followed by microcalorimetry. With NaY (A), the heat of adsorption decreases from 72 $kJ\,mol^{-1}$ initially to 54 $kJ\,mol^{-1}$ after adsorption of 0.2 molecule per supercage, then remains constant up to a value of 5.5 molecules per supercage (i.e., close to that corresponding to a complete filling of supercages: 6 molecules per supercage). With sample D, the heat of adsorption is practically independent on the amount of DCM adsorbed and lower (50 $kJ\,mol^{-1}$) than the value found with sample A. With sample F, the curve is similar to that found with sample A but the values are lower: 64 $kJ\,mol^{-1}$ initially, 50 $kJ\,mol^{-1}$ at the plateau (Fig. 7).

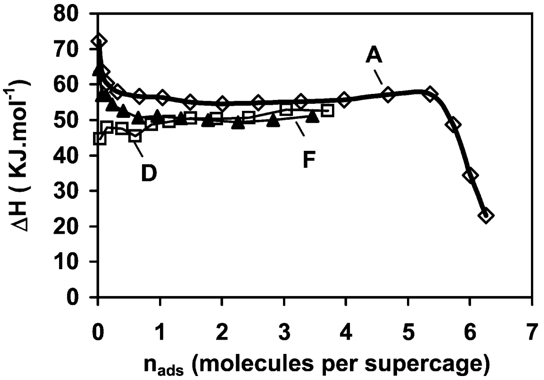


Fig. 7. Differential heat of dichloromethane adsorption as a function of the number of DCM molecules adsorbed per supercage (A) NaY; (D and F) NaY used in DCM conversion with standard feed and in absence of water, respectively.

4. Discussion

The transformation of traces of dichloromethane in wet air was investigated over bifunctional catalysts with Pt and NaY components (PtNaY in which Pt was introduced by exchange of NaY with $Pt(NH_3)Cl_2$, mixtures of NaY and $PtSiO_2$) as well as with pure NaY. With all the catalysts except PtNaY, DCM conversion causes, during the first times of reaction, a change in their physicochemical properties, most likely responsible for the initial deactivation period.

Under the standard conditions: 1000 ppm of DCM, 2.7 mol% water in air, space velocity of 20,000 h^{-1}, a complete conversion of DCM can be obtained at 370–380 °C with all the samples. However, with NaY, formaldehyde, carbon monoxide, and hydrochloric acid are the main reaction products whereas with the bifunctional catalysts except the $PtSiO_2/NaY$ (30/140 mg), there is a complete conversion of DCM into the desired products, i.e., CO_2, HCl, and water. It should be remarked that these samples are more active than all PtHFAU catalysts which were previously investigated under the same operating conditions; a complete conversion of DCM was obtained only for temperatures higher than 420 °C [37]. Although the contact time chosen in this work is generally lower than that chosen by the other authors, the complete conversion of DCM is often obtained at lower temperatures. After the initial period of deactivation, the stability is very high, comparable to that of the best Degussa catalyst [24]. Finally, no chlorinated product can be observed whereas with noble metals supported on alumina, traces of $CHCl_3$ or CCl_4 were found [24].

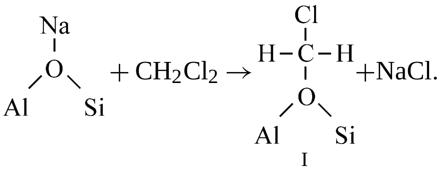
From the effect of temperature on the product distribution, the DCM transformation into CO_2, HCl, and water over the bifunctional catalysts was shown to occur in two successive steps (reaction 2 in part 1–1): hydrolysis of DCM into formaldehyde and hydrochloric acid then apparent direct oxidation of formaldehyde into CO_2 and H_2O. The first step is catalyzed by NaY as shown by the identical conversions of DCM found on NaY pure or added with $PtSiO_2$. The effect of $PtSiO_2$ on CO_2 formation at 300 °C (Fig. 1b) demonstrates that formaldehyde oxidation occurs essentially on the Pt sites. However, at higher temperatures, NaY is able to catalyze the oxidation of formaldehyde successively into CO and CO_2.

Whereas oxidation on Pt sites is well documented, there are very few works related to the hydrolysis of chlorocompounds. Note, however, that chloroform hydrolysis into formic acid was proposed to explain the appearance of a broad OH band around 3580 cm^{-1} and of weak bands at 1711 (C=O), 1605, and 1400 cm^{-1} (O–C–O vibrations) during adsorption on alkali exchanged zeolites [48]. But the formation of formaldehyde during DCM oxidation was never detected. Therefore, the discussion will be focused on DCM conversion into formaldehyde on NaY, the first part dealing with the reaction mechanism over the stabilized sample. In the second part, the modifications of the physicochemical properties of NaY which occur during the transformation of DCM in the presence and absence of water will be examined.

4.1. Mechanism of dichloromethane conversion into formaldehyde

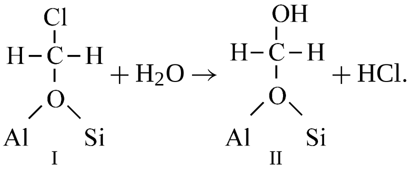
At 300 °C, under standard conditions, DCM is selectively transformed into formaldehyde and hydrochloric acid. After an initial fast deactivation with creation of acidic hydroxyl groups on the catalyst, the activity remains stable on a long period, the catalyst acidity increasing very slowly. Water which is present in the standard feed is indispensable, the products formed initially in the absence of water remaining trapped on the catalyst. The reaction order with respect to DCM and water are equal to 1 and 0, respectively; oxygen is not necessary for formaldehyde production.

The first step of DCM catalytic transformation is most likely the formation of chloromethoxy species by reaction of DCM with an ONa group



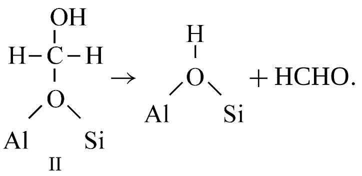
$$\text{Al–O(Na)–Si} + CH_2Cl_2 \rightarrow \underset{\text{I}}{\text{Al–O(CH}_2\text{Cl)–Si}} + NaCl. \quad (4)$$

Alkoxyspecies are currently invoked as intermediates in zeolite catalysis [49–51]. They were identified by NMR not only during the transformation of olefins and alcohols on acidic zeolites, but also during the reactions of halocarbons on alkali, alkaline earth transition metal zeolites [52–54]. Furthermore, the chloromethoxy species I were initially detected by ^{13}C NMR during the transformation of ^{13}C labeled DCM over a ZnY zeolite [55]. In the presence of water, these chloromethoxy species I can undergo a SN_2 substitution leading to HCl and to hydroxymethoxy species II.



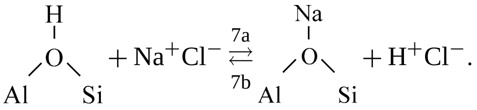
$$\underset{\text{I}}{\text{Al–O(CH}_2\text{Cl)–Si}} + H_2O \rightarrow \underset{\text{II}}{\text{Al–O(CH}_2\text{OH)–Si}} + HCl. \quad (5)$$

Similar reactions, i.e., the hydrolysis of DCM into HCl and chloromethanol (CH_2ClOH) are known to occur in aqueous phase [56]. Species II correspond to formaldehyde molecules adsorbed on protonic sites of zeolites (hemiacetal-like species). Therefore, the desorption of formaldehyde leads to bridging hydroxyl groups, hence to protonic acid sites.



$$\underset{\text{II}}{\text{Al–O(CH}_2\text{OH)–Si}} \rightarrow \text{Al–O(H)–Si} + HCHO. \quad (6)$$

For the formation of formaldehyde to be catalytic (as it was observed on the stabilized sample), the OH groups must be retransformed into ONa groups, which most likely occurs from reaction of OH groups with NaCl liberated by reaction (4).



$$\text{Al–O(H)–Si} + Na^+Cl^- \underset{7b}{\overset{7a}{\rightleftarrows}} \text{Al–O(Na)–Si} + H^+Cl^-. \quad (7)$$

It should be remarked that without step 7, only one HCl molecule would result from transformation of DCM into formaldehyde. Step 7 is reversible as demonstrated by various studies [46]. Obviously, the relative concentrations of the Al–OH–Si and Al–ONa–Si species depend on the relative amounts of Na^+ (NaCl) and H^+ (HCl) species near the OH and ONa groups. Hence, during DCM transformation, the relative mobilities of these species play most likely an important role. The acid strength of the protonic sites (OH groups) is also a determining factor, the equilibrium constant of reaction (7) increasing with acid strength.

The catalytic cycle is plotted in Fig. 8. This catalytic cycle can explain most of the results obtained after the initial period of fast deactivation:

- Formation of two molecules of hydrochloric acid for one molecule of formaldehyde.
- Very good stability of the catalyst verified on a very long period.
- Negligible increase of the protonic acidity.
- Identical rates of formaldehyde formation in the presence or absence of oxygen.

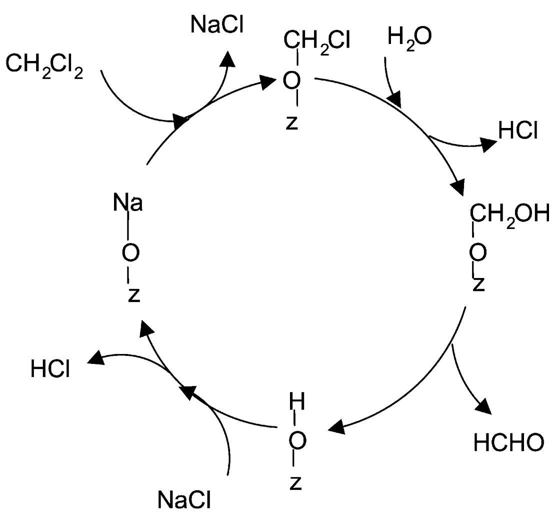


Fig. 8. Scheme of dichloromethane hydrolysis on a NaY zeolite.

In this mechanism, the limiting step is most likely the formation of chloromethoxy species I (reaction (4)). The reaction order equal to 1 with respect to DCM is in agreement with this proposal as well as the zero order with respect to water. Furthermore, adsorption–desorption of formaldehyde over protonic sites can be considered as very easy. Lastly, re-formation of ONa groups can be no more kinetically determining since the amount of hydrochloric acid which is formed is very close to that expected (2 moles for 1 mole of formaldehyde). This latter observation as well as the quasi stability of protonic acidity with time on stream shows also that on the stabilized catalyst, reaction (7) is largely displaced toward the formation of ONa groups.

4.2. Modification of the NaY physicochemical properties during DCM transformation

4.2.1. DCM transformation in the presence of water

A significant decrease of DCM conversion is observed during the first minutes of reaction with the standard feed as well as significant modifications in the composition and in the physicochemical properties of NaY zeolites:

(i) Decrease in the sodium content and retention of Cl and C compounds.
(ii) Elimination of the strongest sites for DCM adsorption.
(iii) Formation of bridging acidic OH groups.
(iv) Dealumination of the framework at a long time on stream.

Modifications (i), (ii) and (iii) can be explained if reaction (7) is strongly displaced toward the formation of bridging OH groups. In this case, DCM transforms through reactions (4)–(6) with formation of one molecule of formaldehyde of HCl and NaCl and of one protonic site per molecule of DCM converted.

$$CH_2Cl_2 + H_2O + NaOZ = HCHO + HCl + NaCl + HOZ. \tag{8}$$

At least two reasons can be invoked to explain this displacement of reaction (7).

1. Only low amounts of Na^+ (NaCl) species would be present at the vicinity of OH groups. Indeed, the migration of NaCl in the catalyst bed is demonstrated by the decrease in Na content (13% after 2 h).
2. Weak acidity of the first OH groups are created and there exists a strong basicity of the first exchanged ONa groups. Indeed it is well known that the average strength of acidic sites increases with the percentage of protonic exchange. Furthermore the strongest adsorption sites, hence the more basic sites, are the first eliminated during DCM conversion (Fig. 7).

The second reason seems the most likely for it could also explain that above a certain degree of exchange, reaction (7) is very displaced toward the formation of ONa groups making catalytic the DCM transformation.

The noncatalytic scheme (reactions (4)–(6)) should lead to the liberation of HCl and formaldehyde (in gas phase) and also of NaCl, part of which being eliminated from the catalyst bed. All these products can be observed but in addition there is retention of C compounds on the catalyst. To explain this observation it can be supposed that during the first minutes of reaction, formaldehyde molecules undergo Cannizaro reaction on the strongest basic sites of NaY with formation of formate species and of methanol. Small bands of formate (at 1385 and 1641 cm^{-1}) were furthermore observed on the stabilized samples. However, the larger part of formate can lead by hydrolysis to formic acid which decomposes into CO_2 (which is initially observed) and H_2 rapidly oxidized into water. Methanol can undergo transformation into light olefins which are rapidly transformed into coke.

From the Na and Cl content of the catalysts, the degree of protonic exchange of NaY can be estimated. Thus after 2 h of reaction (sample D), 13% of the Na atoms were eliminated from the catalyst bed. Furthermore, 1.4 wt% Cl, most likely under the form of NaCl is found in the bed, which corresponds to an additional elimination of 8.5% of the sodium atoms of NaY. Therefore, 21.5% of the Na atoms of NaY were exchanged during DCM transformation with formation of a relatively high number of bridging hydroxyl groups: 960 $\mu mol\,g^{-1}$. Among these sites, only 10% are enough strong to retain pyridine adsorbed as pyridinium ions at 150 °C, which confirms the low acid strength of weakly exchanged NaY samples.

However, a comparison between the concentrations of strong protonic sites of NaY used in DCM transformation and of NaHY samples prepared by conventional protonic exchange [44] shows large differences in favor of the former samples. Thus, sample D has the same number of protonic sites able to retain pyridine adsorbed as a NaHY sample with an exchange degree of 50% [44]. This could be explained by heterogeneity in the degree of exchange of the NaY catalyst, part being exchanged to a high level hence containing a large proportion of strong acid sites, part being weakly exchanged with very few strong acid sites. No longitudinal gradient in acidity was, however, found by characterizing through pyridine adsorption two successive beds of NaY with different granulometrics. This suggests that heterogeneity exists throughout the bed.

The initial decrease in DCM conversion can be explained by elimination of the more basic sites of NaY which are the strongest sites for DCM adsorption. This decrease is less pronounced than the decrease in activity caused by conventional exchange, which is again in favor of heterogeneity in the catalyst bed.

4.2.2. DCM transformation in the absence of water

In the absence of water, there is a continuous decrease in DCM conversion and after 1 h of reaction the catalyst activity is close to 0. Whereas samples D and F that were used 2 h in the presence and absence of water respectively have similar Na and C content, the other characteristics are quite different. Sample F presents:

(i) A higher content in Cl compounds (most likely NaCl), hence a higher degree of protonic exchange: 32% against 21.5% with sample D.
(ii) A much greater concentration of protonic sites: 308 µmol g^{-1} of protonic sites able to retain pyridine adsorbed at 150 °C against 107 over sample D (Table 1).
(ii) OH groups which are not present in sample D. Thus the IR band observed at 3562 cm^{-1} (Fig. 6) is characteristic of OH groups located in the hexagonal prisms. The existence of these OH groups which appear above 60% of protonic exchange by conventional method [44] suggests a very high degree of exchange in at least part of NaY. Furthermore, the band found at 3617 cm^{-1} (Fig. 6) indicates that part of the OH groups created in the supercages interact with extraframework species. DCM conversion has therefore provoked dealumination of the NaY framework.

Volatile chlorinated compounds are known to be able to provoke zeolite dealumination at elevated temperatures ($\geqslant$ 300 °C). Dealumination by phosgene of various protonic zeolites was furthermore demonstrated 20 years ago and a reaction scheme involving successively chemisorption of $COCl_2$ on the protonic sites which release hydrochloric acid then extraction of Al from the framework was proposed. This scheme can be adapted to explain dealumination of NaY by methylene chloride

$$(AlO_2{}^-)Na^+ + CH_2Cl_2 \underset{-NaCl}{\overset{1}{\rightarrow}} (AlO_2{}^-)^+CH_2Cl \overset{2}{\rightarrow} HCHO + AlOCl. \quad (9)$$

Aluminium oxychloride would be removed by reaction with methylene chloride

$$AlOCl + CH_2Cl_2 \rightarrow AlCl_3 + HCHO. \quad (10)$$

Decomposition of the chloromethoxy species resulting from methylene chloride adsorption (step 1, reaction (9)) with framework dealumination was demonstrated by Krawietz et al. [55] to occur on a ZnY zeolite above 150 °C. However, the authors observe the formation of HCl during the decomposition of the chloromethoxy species and propose that dealumination results from Al extraction of the framework by hydrochloric acid. This proposal seems most unlikely, dealumination being observed neither by treatment of NaY in the presence of hydrochloric acid [47] nor during the DCM hydrolysis into formaldehyde and hydrochloric acid (sample D).

However, reactions (9) and (10) cannot explain the significant formation in the absence of water of hydroxyl groups and of the corresponding protonic acid sites. To explain this formation an exchange of Cl of chloromethoxy species (I) by the OH group of NaY silanols with formation of hydroxymethoxy species (II) followed by reaction (6) can be proposed. In agreement with this proposal, the absorbance of the silanol band of sample F was found to be lower than those of NaY (A) and of the samples used in the presence of water (Table 1).

Transformation of DCM in the presence of water (standard feed) of sample F has a significant effect on its physicochemical properties: decrease in Cl content (/3), a large decrease of the bands at 3617 and 3644 cm^{-1} corresponding to acidic hydroxyl groups located in the supercages (Fig. 6) and in the concentration of protonic sites (/3.5), quasi disappearance of the band at 3562 cm^{-1} corresponding to hydroxyl groups of the hexagonal prisms; and increase of the band at 3744 cm^{-1} corresponding to silanol groups (Fig. 6). Reaction (7b) in which hydrochloric acid would result from hydrolysis of $AlCl_3$, DCM, and SiCl groups allows us to explain the decrease in Cl content as well as the decrease in the intensity of OH bands and in the protonic acidity. The significant increase in the silanol band (Fig. 6b) can be related to the hydrolysis of SiCl species. Furthermore, the lower activity in DCM conversion in the presence of water found for the sample G (30% instead of 61% with sample D) can be related to the framework dealumination which occurs during the reaction in the absence of water.

5. Conclusions

The association of Pt sites to NaY lead to highly active and selective catalysts for the catalytic destruction of traces of dichloromethane in wet air. On these catalysts, DCM conversion into the desired products CO_2, H_2O, and HCl occurred through a two-step successive process: DCM hydrolysis on NaY with formation of formaldehyde and hydrochloric acid then complete oxidation of formaldehyde on Pt sites. From the kinetic study of DCM hydrolysis on NaY, a reaction mechanism was proposed involving four successive steps: reaction of DCM on the ONa groups with formation of chloromethoxy species I and liberation of NaCl, hydrolysis of I into hydroxymethoxy species II with liberation of HCl, desorption of formaldehyde with formation of hydroxyl groups and finally recovery of the ONa groups by reaction of NaCl with the hydroxyl groups. Initially, this latter step is largely reversible and DCM transformation does not occur catalytically; acidic hydroxyl groups are formed on NaY by exchange of the strongest basic sites. This exchange was shown to be responsible for the initial period of deactivation. Above a certain degree of exchange, the latter step becomes quasi irreversible, DCM transformation being totally catalytic, the concentration of protonic sites of the catalyst and hence its activity remains quasi constant. In the absence of water, the modifications of NaY are more pronounced: dealumination, creation of a large number of protonic sites, and fast loss in activity.

Acknowledgments

L. Pinard gratefully acknowledges the Agence de l'Environnement et de la Maîtrise de l'Energie and the Région Poitou-Charentes for scholarships.

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