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Journal of Catalysis 221 (2004) 662–665

JOURNAL OF CATALYSIS

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Research Note

Oxidation of chlorinated hydrocarbons over zeolite catalysts
2. Comparative study of dichloromethane transformation over NaX and NaY zeolites

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Received 4 October 2003; revised 16 October 2003; accepted 20 October 2003

Abstract

The transformation of dichloromethane (DCM) was investigated over NaX and NaY zeolites under the following conditions: fixed-bed reactor, 1000 ppm of DCM in wet air, space velocity of 20,000 h^{-1}, temperature between 220 and 450 °C. At short time on stream, there is, with both zeolites, a stoichiometric reaction of DCM and water with the ONa groups, an oxidation of the formaldehyde product, and a significant change in the zeolite physicochemical properties: elimination of the strongest basic sites, creation of OH groups, deposit of NaCl species, etc. After a significant decrease in conversion, DCM transforms catalytically through hydrolysis into HCl and formaldehyde. However, very large differences can be observed between the zeolite samples: higher activity of NaX especially at short times on stream, more pronounced change in its physicochemical properties, etc. Most of these differences can be related to the higher basic strength of the NaX zeolite.

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Keywords: VOCs; Dichloromethane; Hydrolysis; Mechanism; NaX and NaY zeolites; Basicity

In a recent study [1], the complete and selective destruction of traces of dichloromethane (DCM) in wet air was shown to occur at relatively low temperatures ($\geqslant 380\,^\circ$C) over bifunctional PtNaY catalysts. A two-step successive process was demonstrated for DCM transformation: hydrolysis of DCM over the NaY component with production of formaldehyde and HCl followed by the facile and complete oxidation of formaldehyde into CO_2 and H_2O over the Pt sites. Therefore, it can be expected that the substitution of NaY by a more active hydrolysis component will lead to better catalysts for DCM destruction. We show here that it is the case with a NaX zeolite, which can be related to its higher basicity.

The NaX and NaY samples have a Si/Al ratio of 1.3 and 2.45, respectively, and contain 14.4 and 10.5 wt% Na. Pyridine adsorption followed by IR spectroscopy confirms that NaX and NaY have neither protonic acid sites nor Lewis Al sites: no bands corresponding to pyridinium ions (e.g., at 1455 cm^{-1}) or to pyridine coordinated at Lewis Al sites (e.g., at 1545 cm^{-1}) can be observed after pyridine adsorption–desorption at 150 °C. However, bands corresponding to pyridine coordinated to sodium cations [2] are found, the more intense being at 1444, 1491, and 1595 cm^{-1}. The intensity of these bands is approximately 2 times lower with NaY than with NaX. The change in the differential heat of DCM adsorption ($-\Delta H$) with the number of molecules adsorbed per supercage (N) is similar with NaX and NaY, i.e., high values of $-\Delta H$ for low values of N and then a constant value up to a quasicomplete filling of the supercages ($N = 6$). However, the $-\Delta H$ values, hence the strength of DCM adsorption, are significantly higher with NaX than with NaY: initial values of $-\Delta H$ of 140 $kJ\,mol^{-1}$ with NaX compared to 72 with NaY, 64 $kJ\,mol^{-1}$ at the plateau compared to 54 (Table 1), the plateau being obtained for 0.75 DCM molecules adsorbed per supercage instead of less than 0.2 with NaY. These large differences can be explained by considering, as has been proposed by Xie et al. [3], that hydrochlorocarbons adsorb on Na zeolites by both their H and their Cl atoms: hydrogen bonding with basic framework oxygen and interaction of chlorine atoms with Na cations

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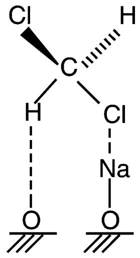
doi:10.1016/j.jcat.2003.10.009

Table 1
Influence of dichloromethane transformation at 300 °C on the physicochemical properties of NaX and NaY

Sample	NaX				NaY			
TOS (min)	0	5	15	120	0	5	15	120
wt%								
C	0	0.2	0.2	0.2	0	0.15	n.d.	0.2
Cl	0	0.25	0.9	5.7	0	0.7	n.d.	1.4
Na	14.4	n.d.	13.2	12.3	10.5	n.d.	n.d.	9.15
n_B (μmol g^{-1})	0	n.d.	337	482	0	72	103	107
$-\Delta H_{ads}$ (kJ mol^{-1})								
Initial	146	64	n.d.	58	72	n.d.	n.d.	50
Plateau	64	64	n.d.	58	54	n.d.	n.d.	50

TOS, time on stream; n_B, concentration of Brönsted sites retaining pyridine adsorbed as pyridinium ions at 150 °C, $-\Delta H_{ads}$ differential heats of DCM adsorption. n.d., not determined.

(Scheme 1):



(1)

Therefore, the stronger adsorption of DCM on NaX would mainly be due to the higher strength of its basic sites. It should, however, be underscored that large differences were also found by Monte Carlo docking calculations between the geometry of adsorbed chloroform molecules on the accessible Na atoms of NaY (only in sites II) and on those of NaX (in sites III and II with a determining role of sites III) [4,5]; in particular, the Cl and Na atoms are in closer proximity with NaX (3.2 Å) than with NaY (3.7 Å).

DCM transformation was carried out in a fixed-bed reactor containing 140 mg of NaX or NaY zeolites. The feed constituted by wet air (2.7 mol% water) containing 1000 ppm DCM was injected at a space velocity of 20,000 h^{-1}. The method used for analysis of reaction products was previously described [1]. Fig. 1a shows that, with both zeolites, there is an initial deactivation followed by a plateau in activity. Whatever reaction temperature and time on stream (TOS), NaX is more active than NaY. Thus, whereas at TOS = 2 min, DCM is totally converted on NaX for temperatures $T \geqslant 220$ °C (Fig. 1a), that occurs on NaY for $T \geqslant 350$ °C only, which indicates a very large difference in activity. On the stabilized samples (TOS = 60 min), the difference in activity is lower: thus at 240 °C, DCM conversion is equal to 36% on NaX and to 9.5% on NaY; i.e., NaX is approximately 4 times more active than NaY.

With the stabilized samples, for $T \leqslant 320$ °C, the only reaction products are formaldehyde and HCl in the 1/2 molar ratio expected from a catalytic DCM hydrolysis:

$$CH_2Cl_2 + H_2O \rightarrow HCHO + 2HCl. \tag{2}$$

On the fresh samples, DCM transformation is much more complex with simultaneous formation of HCHO (as the only desorbed organic product), of HCl, of NaCl species which remain for a large part on the zeolite (see Cl content in Table 1), and of hydroxyl groups on the zeolites (Fig. 2). The formation of these species can be explained by

$$CH_2Cl_2 + H_2O + NaOZ = HCHO + HCl + NaCl + HOZ, \tag{3}$$

which corresponds to a stoichiometric mode of DCM transformation. In addition, part of the formaldehyde product is oxidized into CO_2 and water. This reaction is faster on NaX than on NaY. Thus, with NaX, CO_2 appears for T as low as 220 °C whereas with NaY it appears only above 260 °C. At high temperatures, e.g., 300 °C (Fig. 1b), the yield in CO_2 is always much greater on NaX than on NaY. This oxidation of formaldehyde occurs most likely through the successive 4–6 steps. As neither formic acid nor hydrogen were observed in the reaction products, step 4 would be the limiting step of formaldehyde oxidation

$$HCHO + \frac{1}{2}O_2 \rightarrow HCOOH, \tag{4}$$

$$HCOOH \rightarrow H_2 + CO_2, \tag{5}$$

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O. \tag{6}$$

Catalytic oxidations with molecular oxygen such as reactions (4) and (6) were previously shown to be catalyzed by alkaline zeolites [6–9]. Furthermore, these zeolites and more generally basic oxides are well known to catalyze dehydrogenation of alcohols and even that of formic acid (reaction (5)) rather than their dehydration [10–13]. This oxidation activity of alkaline zeolites would be related to their basic properties, although in certain cases iron impurities could be responsible for part of this activity [14]. HCOOH could also result from the Cannizaro reaction which is known to occur in strongly basic media [15]

$$2HCHO \rightarrow CH_3OH + HCOOH. \tag{7}$$

However, no methanol was observed during DCM transformation on the fresh samples, which makes unlikely this mode of formic acid formation. It should, however, be noted that methanol could be transformed into hydrocarbons and

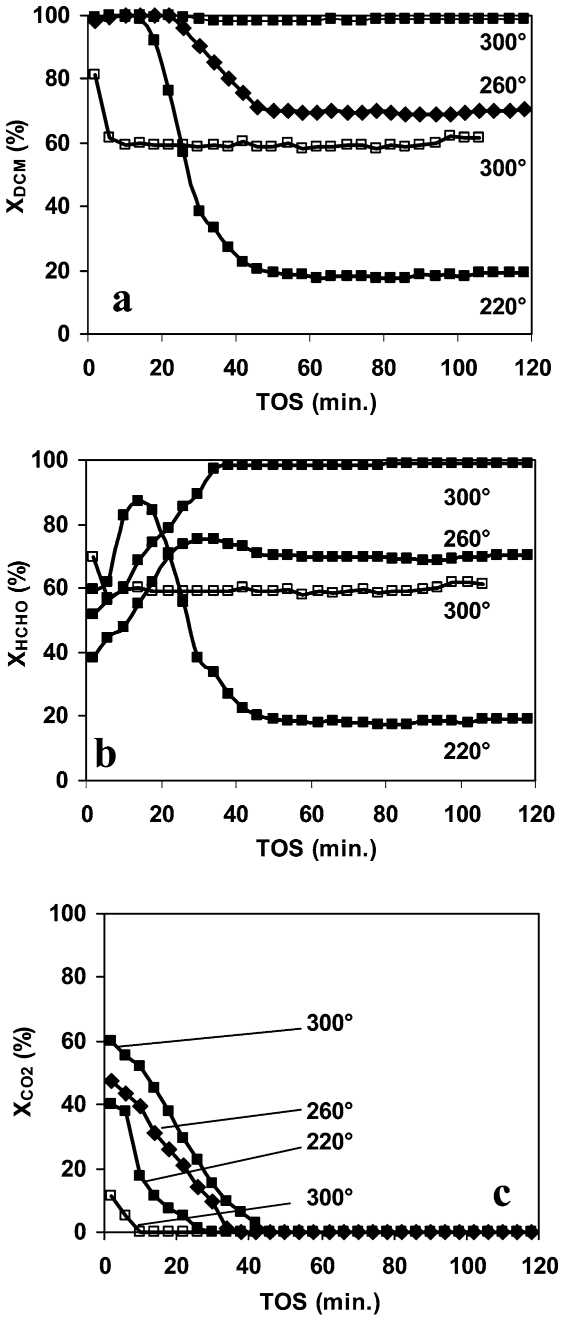


Fig. 1. Transformation of dichloromethane (DCM) over NaX (■) and NaY (□) zeolites. (a) Conversion of DCM (X_{DCM}); (b) yield in formaldehyde (X_{HCHO}); (c) yield in CO_2 (X_{CO_2}) as a function of time on stream (TOS).

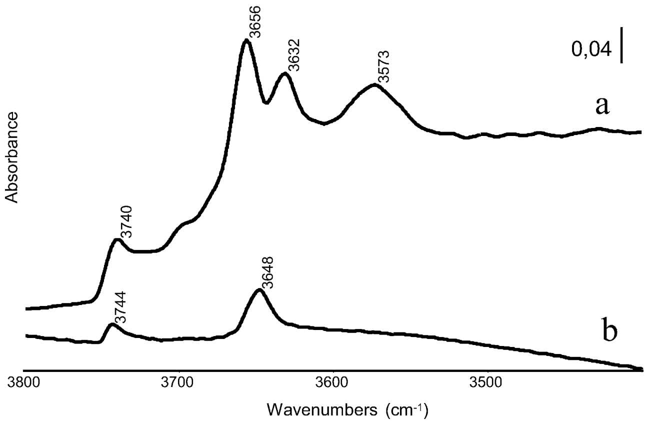


Fig. 2. IR spectra in the hydroxyl region for NaX (a) and NaY (b) samples used for 120 min in dichloromethane transformation.

even coke on the protonic sites which are created in the first minutes of reaction (Table 1).

The higher activity of the fresh NaX sample observed for DCM conversion and for CO_2 formation (Fig. 1) is confirmed (in agreement with Eq. (3)) by (i) the greater deposit of chlorine species: e.g., 4 times greater on NaX than on NaY after 2 h reaction at 300 °C (Table 1); (ii) the more significant formation of hydroxyl groups (Fig. 2) and of protonic sites (Table 1). Thus, after 2 h reaction, the concentration of protonic sites able to retain pyridine adsorbed at 150 °C is 4.5 times greater with NaX than with NaY. This higher activity can be related to the higher strength of DCM chemisorption on the more basic sites of the NaX zeolite. The stronger H_{DCM}–O_{zeolite} interaction has probably two positive effects on the rate of DCM hydrolysis. On one hand, the concentration of chemisorbed DCM species on NaX should be greater than on NaY, on the other, the scission of the C–Cl bond with formation of NaCl could be facilitated. In addition, the closer proximity of Cl and Na atoms in the DCM species chemisorbed on NaX [4,5] could have a positive effect on the scission of the C–Cl bond.

With both zeolites, there is a large initial decrease in CO_2 production and after 10 min (NaY) or 30–40 min of reaction (NaX), no CO_2 can be observed in the reaction products (Fig. 1c). The change in formaldehyde production (Fig. 1b) depends both on the zeolite and on the reaction temperature: with NaY at 300 °C, there is a small initial decrease whereas with NaX there is a significant increase followed by a plateau at 260 and 300 °C and a maximum at 220 °C. With this latter zeolite, the initial increase in formaldehyde production can be related to the decrease in CO_2 production. This confirms the secondary oxidation of formaldehyde into CO_2 and suggests that the oxidation sites are more sensitive to deactivation than those involved in DCM hydrolysis.

The stabilization period also causes a significant change in the strength of DCM chemisorption. Thus, with both NaX and NaY samples, the stronger chemisorption sites disappear during this period: the initial values of the heat of DCM chemisorption ($-\Delta H_{\mathrm{ads}}$, Table 1) pass from 146 kJ mol^{-1} with the fresh NaX sample to 64 and 58 kJ mol^{-1} after 5 and 120 min reaction; with NaY, $-\Delta H$ passes from 72 kJ mol^{-1} with the fresh sample to 50 kJ mol^{-1} after 120 min reaction (Table 1). The higher value obtained on the stabilized NaX sample suggests a stronger basicity of this zeolite in agreement with its higher activity.

As indicated above, hydroxyl groups are created during the stabilization period, their number being more significant with NaX than with NaY. Differences also exist in the type of hydroxyl groups formed with NaX and NaY. Thus, with NaX, five IR OH bands appear instead of two with NaY

(Fig. 2). The common OH bands can be ascribed to silanol groups (3742–3744 cm^{-1}) and bridging OH groups in the supercages (3649–3656 cm^{-1}). The additional bands found with NaX correspond to OH groups of extraframework species (3696 cm^{-1}), to supercage OH groups in interaction with extraframework Al species (3632 cm^{-1}), and to bridging OH groups in the hexagonal prisms (3573 cm^{-1}) [2]. The presence of this latter band shows that the exchange of NaX is not limited to the Na cations accessible to DCM molecules but also occurs in sites I and I′. This exchange which cannot result from reaction of ONa groups with DCM molecules is most likely due to the well-known redistribution of Na cations and protons in the zeolite lattice which is particularly favored under the operating conditions of DCM transformation (relatively high T, presence of water). Furthermore, the presence of the band at 3696 cm^{-1} corresponding to hydroxylated extraframework Al species indicates a partial dealumination of the NaX sample. This higher sensitivity of the X zeolite to dealumination could be expected from its low Si/Al ratio.

There is also a very significant difference between NaX and NaY samples in what concerns the effect of the stabilization period on the IR bands corresponding to pyridine coordinated to the Na cations of the supercages. Over NaX, the band at 1444 cm^{-1} has completely disappeared after 2 h reaction whereas a decrease of only 10% is found with NaY. Therefore, on the stabilized NaX catalysts, DCM hydrolysis should occur on the OH groups of the supercages,

$$\begin{aligned}&\mathrm{ZOH} + \mathrm{CH_2Cl_2} \xrightarrow{-\mathrm{HCl}} \mathrm{ZOCH_2Cl_2} \xrightarrow[-\mathrm{HCl}]{\mathrm{H_2O}} \mathrm{ZOCH_2OH}\\ &\quad \rightarrow \mathrm{ZOH} + \mathrm{HCHO}, \qquad (8)\end{aligned}$$

and not on the ONa groups as was the case with the stabilized NaY sample. However, the percentage of protonic exchange of the NaX sample used for 2 h in DCM transformation, estimated either from the elemental composition (36%) or by comparison of its acidity (n_B, Table 1), with that of NaHX samples prepared by conventional exchange (50%) is lower than the percentage of Na atoms in sites II and III of NaX (69%). This suggests that ONa groups still exist in the supercages but are unable to interact with pyridine molecules probably because of the presence at their vicinity of several protonic sites (3 to 4 protonic sites per supercage for 36–50% of protonic exchange). The access of pyridine to the ONa groups could also be limited by the presence of nearly three NaCl species (most likely dissociated into Na^+ and Cl^- ions [16]) in each supercage of this NaX sample. Therefore, it is quite possible that DCM hydrolysis on the stabilized NaX samples occurs on ONa groups as is the case on the stabilized NaY sample.

As a result of the very positive effect of basicity on the rate of DCM hydrolysis which is shown in this paper, very active, stable, and selective bifunctional catalysts formed by association of basic zeolites with an oxidizing component can be proposed for the destruction of chlorinated volatile organic compounds [17]. For instance, the association of Pt with NaX was shown to lead to stable catalysts capable of completely transforming DCM into CO_2, H_2O, and HCl above 330 instead of 380 °C with Pt NaY catalysts [17].

Acknowledgments

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

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