Catalysis Letters 7 (1990) 409–416

HETEROGENEOUS CHLORINATION OF FORMALDEHYDE WITH HCl IN THE PRESENCE OF ZEOLITE Y

Iwona BRESIŃSKA [1],* and R.S. DRAGO [2]

[1] *A. Mickiewicz University, Faculty of Chemistry, 60-780 Poznań, Grunwaldzka 6, Poland*
[2] *University of Florida Department of Chemistry, Gainesville Florida 32611, U.S.A.*

Received 2 July 1990; accepted 12 September 1990

Zinc substituted zeolite Y is a potential catalyst in the CH_2Cl_2 formation in a one step gas phase reaction of CH_2O with CHl. Methanol and dimetoxymethane are suggested as possible intermediates in the formation of CH_3Cl and CH_2Cl_2. The decomposition pathway of CH_2O on zeolites seems to play an important role in the chlorination reaction mechanism. A certain combination of such factors as temperature, catalyst acidity and cation action must occur in order to activate CH_2O molecules for the reaction with HCl. The chlorination reaction is accompanied by side reactions resulting in the formation of nonchlorinated compounds such as methyl formate, ethers, aldehyde.

1. Introduction

The chemistry of formaldehyde in aqueous solution is well investigated [1], but limited data are available on the reactions of formaldehyde over zeolites [2–9]. In water solution, formaldehyde reacts with HCl resulting in the formation of dichloromethyl ether [1], whereas in the presence of alkali metal zeolites formaldehyde is converted mainly into methyl chloride [10]. In this study we focused our attention on the feasibility of formaldehyde conversion to methylene chloride with HCl used as a chlorinating agent.

2. Experimental

MATERIAL

NaY(Na_2O-13%, SiO_2-63.8%, Al_2O_3-22.9%) zeolite was obtained from Union Carbide Co. Other cationic forms were obtained by an aqueous-ion exchange of NaY zeolite in 0.25M solutions of chloride salts. The hydrogen form was prepared by thermal decomposition of its ammonium form at 623 K in a nitrogen

---

* To whom the correspondence should be addressed.

flow. The extent of exchange was determined by atom absorption on solids dissolved in strong acids. CuY was exchanged in 80%, FeY-67%, ZnY-67%.

Hydrogen chloride (Matheson 99.5%) was used without further purification. Nitrogen carrier gas was dried over zeolite A. Formaldehyde gas was generated by heating paraformaldehyde at 348 K in an oil bath.

PROCEDURE

The zeolites were activated by heating at 623 K for 4 hours under a dry nitrogen flow, then cooled down up to 373 K and formaldehyde was preadsorbed for 4 hours prior to the chlorination reaction. Former tests proved a favorable effect of such a pretreatment on the catalysts activity [10].

The chlorination reactions were carried out at 373–673 K in a continuous flow system equipped with calibrated flow-meters for HCl and N_2. The formaldehyde content in the reaction feed was established by the absorption of effluent gas from the generator into two water scrubbers. The resulting formaldehyde solution was analyzed by the sulfite method [1]. By keeping the constant conditions (N_2 flow through a generator, the oil bath temperature) a consistent feed of CH_2O was possible. All tubings were heated to about 363 K to prevent formaldehyde condensation.

In a typical run, the reactor feed contained HCl (6.6 vol.%) and CH_2O (0.73 vol.%), i.e. the molar ratio was 9 : 1, carried in a nitrogen stream. The contact time was 7×10^{-3} h, the charge rates were 0.0982 mmole/h for CH_2O and 0.892 mmole/h for CHl per gram of the catalyst. The reaction product mixture was analyzed by gas chromatography using a Porapak Q packed column at 403 K and a FID detector, so only organic compounds were monitored. A TC detector could not be used during permanent tests, because it underwent passivation in the presence of HCl and water, and became insensitive. Products were quantatively estimated by comparing the GC peak heights to the calibration curves. The product yields (mole%) were calculated on the basis of formaldehyde content in the gas feed.

3. Results and discussion

Formaldehyde in acid solutions is converted into methylal type derivatives [1] and such compounds could be byproducts in CH_2Cl_2 formation. It seems that in the heterogeneous process the HY zeolite meets all the requirements set for this reaction. It has got strong Broensted acid sites and its framework is stable under acid conditions which could be due to the presence of water, formed during the chlorination reaction and the presence of HCl in the reaction feed. When the reaction feed passes the empty glass reactor, heated to 373 K, methyl chloride and methyl formate were formed in trace amounts 2×10^{-4} mole% and 2×10^{-3} mole%, respectively.

Table 1
Activities of zeolites for the chlorination of formaldehyde at 373 K and 673 K (yields after 1 hour reaction)

Catalyst	Product yields (mole%)			
	373 K		673 K	
	CH_3Cl	$HCOOCH_3$	CH_3Cl	CH_2Cl_2
HY	3	0	12	0
CuY	2	15	2	0
FeY	8	2	9	0
ZnY	43	5	16	8
Al_2O_3	6	12	32	0

In the reaction of CH_2O with HCl over HY zeolite at 373 K the only chlorinated product was methyl chloride with yield ~ 2 mole% in the reaction stationary state, and traces of dimethyl ether could be observed. The rise in the reaction temperature up to 673 K did not alter the products distribution, it only increased the CH_3Cl formation to 12 mole% in the stationary state (table 1). Our attempts to form CH_2Cl_2 over HY zeolite under other reaction condition (different temperature, molar ratio $CH_2O:HCl$, contact time) have failed as well. Therefore, we took into consideration transition metals known as components of chlorination catalysts. Substitution of Na cations in zeolites for polyvalent cations is accompanied by the generation of Broensted acid sites [11]. In this case, Broensted acidity and cationic sites action could be considered as factors responsible for the catalyst activity. Copper, iron, zinc forms of Y zeolite were tested at 373 and 673 K for their catalytic activity in the chlorination of CH_2O.

Table 1 briefs the results of the tests, but it does not include products which were observed in amounts smaller than 1 mole%. As in the case of HY, methyl chloride appeared to be a major chlorinated product regardless of the reaction temperature and the nature of cation introduced into zeolite. Depending on the cation present in zeolite, other products were detected at 373 K.

Methyl formate was formed as the only additional product over CuY or in a fair amount on FeY and ZnY (table 1). The presence of methyl formate over cationic forms of Y zeolite points to the occurrence of the dimerization of CH_2O

$$2CH_2O \rightarrow HCOOCH_3 \qquad (1)$$

in which cationic sites of zeolite are probably involved. The absence of such a compound over HY zeolite (where only traces of dimethyl ether were observed) can account for the lack of cationic sites. Dimethyl ether (on FeY, ZnY), ethanol and diethyl chloride (on FeY) in trace amounts were found as additional products.

Among the catalysts studied, ZnY is the most active and promising catalyst. On this particular catalyst, CH_2O is converted to CH_3Cl at 373 K (43 mole%), at

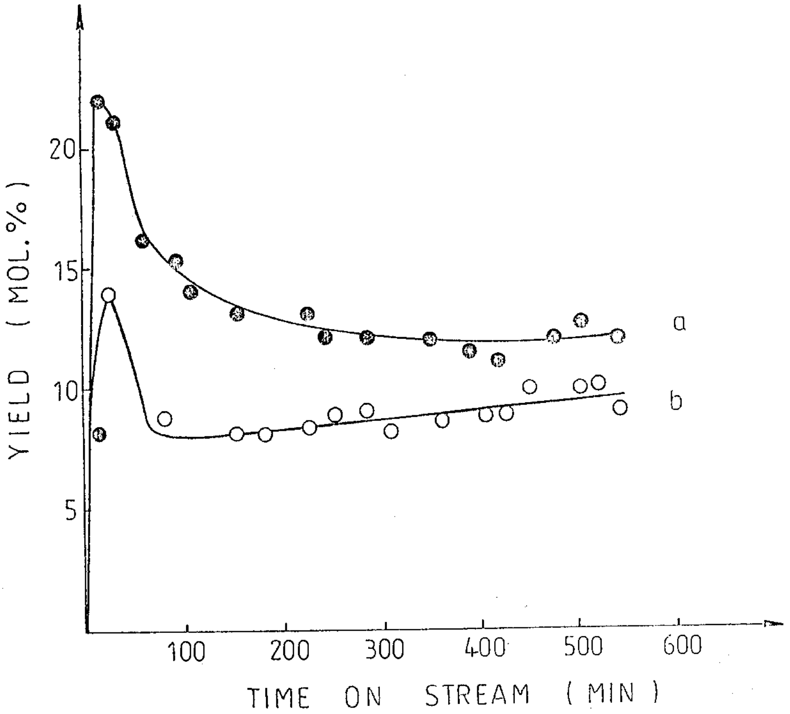

Fig. 1. The formation of CH_3Cl and CH_2Cl_2 over zeolite ZnY at 673 K. a–●–CH_3Cl yield, b–○–CH_2Cl_2 yield.

673 K to methyl (16 mole%) and methylene (8 mole%) chlorides after 1 hour reaction (see table 1). The CH_3Cl yield at 373 K drops to 22 mole% after 6 hours on stream which suggests the deactivation of the catalyst by HCl. It might be considered that the high activity of ZnY results from the catalytic action of $ZnCl_2$ deposited inside zeolite cavities. $ZnCl_2$ in the presence of HCl forms $ZnCl_4^{2-}$ and H^+ and then acts in the way similar to that of the Friedel-Crafts reaction catalyst [12]. Literature data [2] have shown that at a low temperature, HCl substitutes the cations in NaY zeolite and the deposition of salts in cavities takes place. Therefore, the sample of $ZnCl_2$ was tested for its performance in the $CH_2O + HCl$ reaction at 373 K. The product distribution (0.2 mole% of CH_3Cl, 20 mole% of $HCOOCH_3$) differs significantly from that observed on ZnY zeolite. The CH_3Cl to $HCOOCH_3$ ratio in the products on ZnY was 9 : 1, whereas in the case of ZnCl it was 1 : 100. It is evident from these results that the catalytic activity in CH_3Cl formation does not originate from $ZnCl_2$ possibly deposited in zeolite.

Fig. 1 illustrates the catalytic activity of ZnY zeolite at 673 K. Over this catalyst methyl and methylene chlorides are the main products of the reaction studied. Small amounts of acetaldehyde (less than 1 mole%) and traces of unidentified species were formed as well.

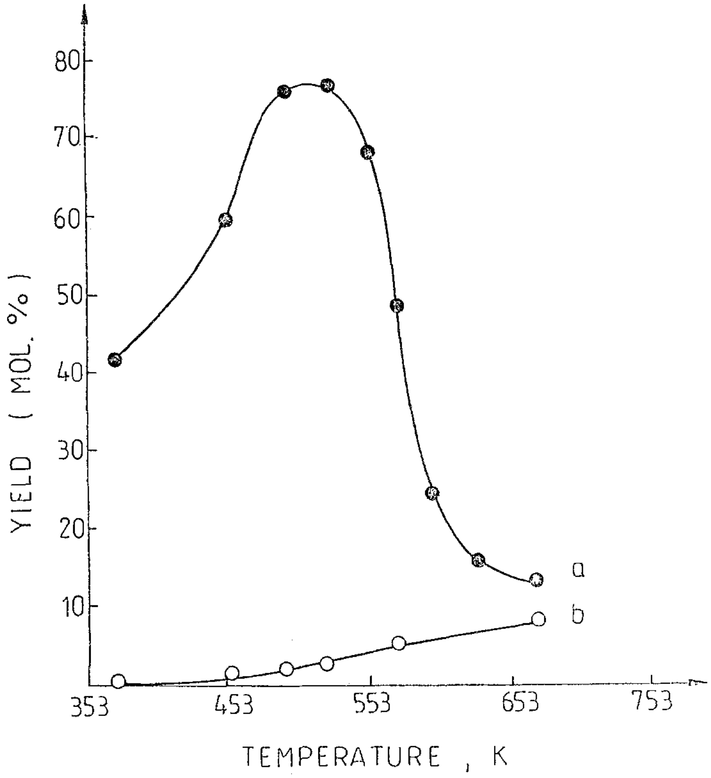

Fig. 2. Activity of ZnY for the chlorination of CH_2O at different temperatures (after 1 h on stream). a–●–CH_3Cl yield, b–o–CH_2Cl_2 yield.

The chlorination reaction competes with the decomposition of CH_2O itself, and significant coking of the catalyst occurs. As the reaction progresses, the catalyst particles get stuck together and turn black. The elemental analysis of the ZnY after 40 hours on a stream revealed the 5.24% of carbon and 0.75% of H. In spite of coking (fig. 1), the ZnY activity is stable for a long time, (with an increasing tendency in the CH_2Cl_2 formation up to 12 mole% during 40 hours on a stream). A shorter contact time (1.4×10^{-3} h/at 673 K diminishes the yields of methyl and methylene chloride in the stationary state of 6 mole% and 3 mole%, respectively. Changes in the reaction course over ZnY with the temperature arouse our interest and encouraged us to study this catalyst in detail. As follows from fig. 2, the catalytic activity of ZnY strongly depends on the reaction temperature. The CH_3Cl yield approaches its maximum at 473–523 K (curve a) and is accompanied by the diminishing of $HCOOCH_3$ production and the formation of dimethyl ether.

The industrial methods of methyl chloride production consists in the chlorination of methane with chlorine or with HCl in the presence of O_2 [14,15]. However, in our case, this path can be excluded because of methane absence, even in trace amounts, in the reaction products or during the adsorption of CH_2O over the catalysts studied.

Patent data [16–21] point to the possibility of methyl chloride manufacture from methanol and HCl in this temperature range over zinc-containing solid catalysts. This fact and the presence of by products such as dimethyl ether and methanol after the reaction over ZnY and other zeolites suggests that methanol or methoxy species could act as intermediates during the reaction of CH_3Cl formation. The CH_2Cl_2 formation over ZnY starts above 473 K and increases with the reaction temperature (curve b, fig. 2) at the cost of $HCOOCH_3$. This fact suggests that at higher temperatures methyl formate may undergo further reactions, for example

$$HCOOCH_3 + CH_2O + H_2O \rightarrow 2CH_3OH \tag{2}$$

$$2CH_3OH + CH_2O \rightarrow CH_3OCH_2OCH_3 \tag{3}$$

Previously, dimethoxymethane species were found after CH_2O adsorption on solids [22–24] and NH_4Y zeolite [10]. When NH_4Y was employed as a catalyst in the $CH_2O + HCl$ reaction, both methyl and methylene chlorides were observed [10]. Over ZnY zeolite at higher temperatures the presence of such a species or its decomposition products i.e. $CH_2(OH)_2$ and CH_3OH cannot be ruled out, all the more because CH_3Cl/CH_2Cl_2 molar ratio is about 2 in the reaction products at 673 K, where we were not able to detect even traces of $HCOOCH_3$. Our findings together with the already mentioned formation of dimethoxymethane during the adsorption of CH_2O on NH_4Y suggest that dimethoxymethane could be a possible intermediate in the CH_2Cl_2 formation via the following step:

$$CH_3OCH_2OCH_3 + 4HCl \rightarrow CH_2Cl_2 + 2CH_3Cl + 2H_2O \tag{4}$$

We would like, however to emphasize that our explanation of the reaction course on ZnY zeolite in higher temperatures is only tentative. A study of the identification of the reaction intermediates and their exact role in the chlorination mechanism is under way in order to confirm the above interpretation.

4. Conclusions

According to the results of our investigation, it is possible to obtain CH_2Cl_2 from CH_2O and HCl in a one step gas phase process, though a mixture of products in formed. The zinc substituted zeolite has met our aim in the closest way. Our results clearly show that the reaction studied is not a simple conversion of aldehyde into the chlorinated derivatives. Formaldehyde interacts with zeolite resulting in the formation of intermediates which are consecutively transformed into chlorinated derivatives. On the other hand these intermediates can undergo further reaction leading to the byproducts such as ethers, alcohols, aldehyde. The methanol or methoxy-containing species are proposed as reaction intermediates in the methyl chloride formation. We also believe that dimethoxymethane or products of its acidic hydrolysis are the potential intermediate species responsible for the methylene chloride presence.

Acknowledgment

The authors would like to acknowledge support of this research by the National Science Foundation through Grant 86-18766.

References

[1] J.F. Walker, *Formaldehyde* (Reinhold Publishing Corporation, New York, 1953).
[2] P.B. Venuto and P.S. Landis, Adv. Catal. 18 (1968) 259.
[3] T. Yashima, K. Sato, T. Hayasaka and N. Hara, J. Catal. 26 (1972) 303.
[4] S. Trigerman, E. Biron and A.H. Weiss, React. Kinet. Catal. Lett. 6 (1977) 269.
[5] M.L. Unland, J. Phys. Chem. 82 (1978) 580.
[6] M.D. Sefcik, J. Amer. Chem. Soc. 101 (1979) 2164.
[7] A.H. Weiss, S. Trigerman, G. Dunnells, V.A. Likholobov and E. Biron, Ind. Eng. Chem., Process Res. Dev. 18 (1979) 522.
[8] F. Seel, W. Schaum and G. Simon, Z. Naturforsch. 36b (1981) 1451.
[9] F. Seel, A. Dessauer, G. Simon and V. Eder, Z. Naturforsch. 37b (1982) 1540.
[10] I. Bresińska and R.S. Drago, Catal. Lett. 7 (1990).
[11] D.W. Breck, *Zeolite Molecular Sieves* (Wiley-Interscience, New York, London, 1974).
[12] R.T. Morisson and R.N. Boyd, *Organic Chemistry*, third edition, Polish translation (PWN, Warszawa, 1985).
[13] Japan Kokai 76, 118, 707, 18 Oct. 1976 (Chem. Abstr. 86 (1977) 120770y).
[14] P. Weisman, *An Introduction to Industrial Organic Chemistry* (Applied Science Publishers, Ltd, 1972) p. 137.
[15] S. Ropuszyński, *Chemistry and Technology of Organic Synthesis*, in Polish (PWN, Warszawa, 1988) p. 159.
[16] Japan Kokai 77, 05, 702, 17 Jan. 1977 (Chem. Abstr. 86 (1977) 189178d).
[17] Japan Kokai Tokkyo Koko JP81, 127, 324, 06Oct 1981 (Chem. Abstr. 96 (1982) 6147g).
[18] Ger. Offen. DE 3, 110, 65, 30 Sep. 1982 (Chem. Abstr. 98 (1983) 4275g).
[19] Japan Kokai Tokkyo Koko JP 58, 27, 644, 18 Feb. 1983 (Chem. Abstr. 99/1983) 70183e).
[20] Ger (East) DD 237, 065, 02 Jul. 1986 (Chem. Abstr. 107 (1987) 96318m).
[21] Ger (East) DD 237, 058, 02 Jul. 1986 (Chem. Abstr. 107 (1987) 136308s).
[22] H. Ai, J. Catal. 83 (1983) 141.
[23] G. Busca, J. Lamotte, J.C. Lavalley and V. Lorenzelli J. Amer. Chem. Soc. 109 (1987) 5197.
[24] H. Idriss, J.P. Hidermann, R. Kieffer, A. Kiennemann, A. Vallet, G. Chauvin, J.C. Lavalley and P. Chaumette, J. Mol. Catal. 42 (1987) 205.