Catalysis Letters 7 (1990) 403–408

GAS PHASE REACTION OF FORMALDEHYDE AND HYDROGEN CHLORIDE IN THE PRESENCE OF ZEOLITE Y

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Received 16 July 1990; accepted 14 September 1990

The hydrogen and metal alkali forms of Y zeolite were tested in chlorination of CH_2O with HCl. It has been found that over alkali metal and hydrogen forms the only chlorinated product was methyl chloride, whereas in the presence of NH_4Y zeolite both methyl and methylene chlorides were formed. The conversion pathway of CH_2O itself seems to play an important role in the chlorination reaction mechanism. Methanol or methoxy species and dimethoxymethane are suggested as possible intermediates in the formation of CH_3Cl and CH_2Cl_2.

1. Introduction

In many heterogeneous reactions formaldehyde has been found to react in the same way as it does in aqueous solutions. The Cannizzaro reaction [1], conversion into formose sugars [2–4] or glycoealdehyde [5] and alkylation of toluene with CH_2O [6] have proceeded in the presence of zeolites. In water, formaldehyde reacts with HCl yielding chloromethyl ethers [7].

We were interested in determining whether zeolites could catalyze the addition of HCl to the carbonyl group of formaldehyde. Such one step process would open a new route in the industrial production of methylene chloride.

2. Experimental

MATERIALS

$NH_4Y((NH_4)_2O$–4%, Na_2O–0.2%, SiO_2–72.2%, Al_2O_3–22.8%) was supplied by Alfa Products. $NaY(Na_2O$–13%, SiO_2–63.8%, Al_2O_3–22.9%) zeolite was obtained from the Union Carbide Co. The hydrogen form of zeolite Y was prepared by thermal decomposition of its ammonium form at 623 K for 4 hours in a nitrogen

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flow. The other cationic forms were obtained by aqueous-ion exchange of NaY zeolite in 0.25M solutions of chloride salts.

After washing and drying at 373 K in vacuo, zeolites were stored in a dessicator containing an NH_4Cl solution, to equilibrate the water content. The extent of exchange was determined by atomic absorption on solids dissolved in strong acids. LiY was 50% exchanged, KY–49%. 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, all but one (NH_4Y), prior to the reaction were heated at 623 K for 4 hours under a dry nitrogen flow. In the case of NH_4Y such an activation procedure in not suitable because of zeolite deammination in high temperatures. This particular catalyst was heated at 435 K.

The experiments were carried out mainly at 373 and 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 in two water scrubbers. The resulting formaldehyde solution was analyzed by the sulfite method [1]. By keeping conditions (N_2 flow through a generator, the oil bath temperature) constant, a consistent feed of CH_2O was possible.

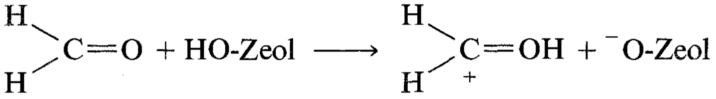
All tubings were heated to ~ 363 K to prevent formaldehyde condensation. In a typical run, the reactor feed contained HCl (6.6 vol.%) and CH_2O (0.73 vol. %), i.e. molar ratio was 9 : 1, carried in a nitrogen stream. The contact time was 7×10^{-3} h, the charge rates were 0.0982 mmole/h for CH_2O and 0.892 mmole/h for HCl 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 the permanent tests, because it underwent passivation in the presence of HCl and water and became insensitive. The products were quantitatively estimated by comparing the GC peak heights to the calibration curves. The product yields (mole%) were calculated on the grounds of formaldehyde content in the gas stream.

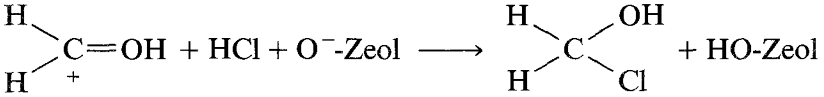
In several cases, gaseous products were identified by GS MS method using TC detector and Porapak Q packed column.

3. Results and discussion

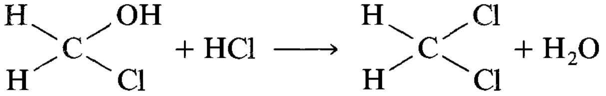
The heterogeneous process of HCl addition to the carbonyl group of formaldehyde and the subsequent conversion of the resulting hydroxyl group to a chloro group would require a strong acid catalyst. The catalyst should be also stable in the acidic environment which would arise from the presence of water, formed during the reaction and HCl present in the reaction feed. It appears that zeolite HY meets all the above requirements. The HY zeolite has got strong Broensted acid sites and its framework is stable under mild acid conditions (pH ~ 2.5–3). The following reaction pathway might be considered possible if zeolite HY is employed as a catalyst



$$H_2C{=}O + \text{HO-Zeol} \longrightarrow H_2C{=}\overset{+}{O}H + {}^{-}\text{O-Zeol} \qquad (1)$$



$$H_2C{=}\overset{+}{O}H + HCl + O^{-}\text{-Zeol} \longrightarrow H_2C(OH)Cl + \text{HO-Zeol} \qquad (2)$$



$$H_2C(OH)Cl + HCl \longrightarrow H_2CCl_2 + H_2O \qquad (3)$$

During the reaction over zeolite HY at 373 K methyl chloride was formed with very low yield 0.3 mole% at the reaction stationary stage and traces of dimethyl ether were observed as well. However, when the catalyst was pretreated with CH_2O at 373 K for 4 hours prior to the chlorination reaction, the CH_3Cl yield increased 8 times, to about 2 mole% at the reaction stationary state. The favorable effect of the pretreatment with CH_2O has encouraged us to pretreat the other zeolites in the similar way, prior to their use in the chlorination reaction.

The rise in the reaction temperature up to 673 K has not altered the chlorinated product distribution, it has only increased the CH_3Cl formation to 12 mole% in the stationary state (table 1).

Contrary to the assumption mentioned above, the chlorination of CH_2O over HY does not lead to the formation of methylene chloride. Our attempts to form

Table 1
Activities of cation exchanged zeolites for the chlorination of formaldehyde at 373 and 673 K

Catalyst	Product yields (mol%)				
	373 K			673 K	
	CH_3Cl	CH_2Cl_2	$HCOOCH_3$	CH_3Cl	CH_2Cl_2
HY	3	0	0	12	0
KY	6	0	6	18	0
NaY	4	0	4	22	0
LiY	3	0	2	24	0
NH_4Y *	6	6	2	–	–
	(All yields were calculated after 1 h of reaction)				

Prior to reaction catalysts were activated at 623 K and pretreated with CH_2O at 373 K for 4 h.
* NH_4Y was activated at 453 K to prevent from decomposition to HY and pretreated with CH_2O at 373 K.

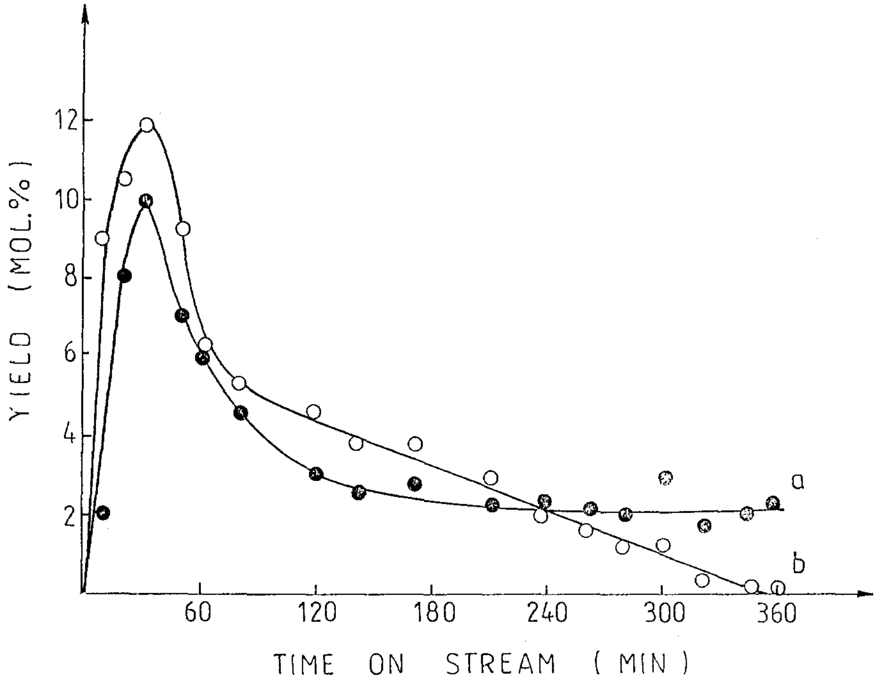


Fig. 1. Activity of NH_4Y at 373 K. a -●- CH_3Cl yield, b -○- CH_2Cl_2 yield.

CH_2Cl_2 over HY, LiY, NaY, KY zeolites even under other reaction conditions (different temperature, molar ratio of $CH_2O:HCl$, contact time) have failed as well. Over alkali metal zeolites at 373 K besides methyl chloride, methyl formate could be detected during the initial reaction period. The presence of methyl formate indicates that the chlorination reaction competed with the conversion of formaldehyde itself either via the Cannizzaro

$$2CH_2O + H_2O \longrightarrow CH_3OH + HCOOH \longrightarrow HCOOCH_3 \quad (4)$$

or the Tischenko reaction

$$2CH_2O \longrightarrow HCOOCH_3 \quad (5)$$

With the reaction progress the CH_3Cl and $HCOOCH_3$ formation gradually decreased, the CH_3Cl yield reached the stationary state 2 mole% as was observed in HY case, whereas the $HCOOCH_3$ formation ceased after about 6 hours on stream. At a high temperature (673 K) alkali metal forms were more active in CH_3Cl formation than HY (table 1). Only in the presence of NH_4Y, both chlorinated derivatives (fig. 1) and methyl formate were found in the reaction products.

On this particular catalyst at 373 K methyl and methylene chlorides were formed with yields of 6 mole% each (after 1 h reaction). However, methylene chloride and methyl formate contents in the products mixture diminished as the reaction progressed and after 6 hours on stream the catalyst stops to be active in the formation of CH_2Cl_2 and $HCOOCH_3$. On the other hand the CH_3Cl yield approaches the stationary state (~ 2 mole%) as previously observed for HY zeolite.

The decay of catalytic activity of cationic forms of zeolites 373 K is due to the transformation into the hydrogen form.

It has been shown [1,6,8–10] that the interaction of HCl with zeolites is temperature dependent. At low temperatures H^+ replaces Na^+ in NaY zeolite [1] leading to occluded salts, whereas in high temperatures HCl interacts reversibly with cations without ion exchange [6,9,10]. The same phenomena can account for the reactivity observed in the reaction of CH_2O with HCl over the zeolites studied. At 373 K the activity of catalyst containing cations in the reaction stationary state and HY zeolite is the same whereas at a high temperature (673 K) alkali metal forms are more active (see table 1). For NH_4Y zeolite after 6 hours on stream the nitrogen content was lowered twice when compared to the original sample (1.18% and 2.13% respectively), which indicated the removal of NH_4^+ from zeolite probably by water, one of the reaction products. In the IR spectra of this catalyst the band corresponding to NH_4^+ around 1410 cm^{-1} was still present and was probably due to NH_4Cl deposited in zeolite. After heating the sample at 673 K in air stream the NH_4Cl solid was deposited on the reactor walls.

The changes in products distribution in the reaction of CH_2O with HCl over NH_4Y and HY zeolites induced us to follow the adsorption of CH_2O and the chlorination reaction in detail, using the GCMS method.

Table 2 summarizes the results. Adsorption of CH_2O on HY and NaY zeolites seems to follow the literature patterns [1,6,11,12]. Close examination of products evolved after adsorption and in the chlorination reaction allowed us to draw some conclusions as to the pathway of the reaction studied.

After adsorption of CH_2O over NH_4Y zeolite methyl formate and dimethoxymethane is found. In the initial period of the reaction $CH_2O + HCl$ over NH_4Y methyl and methylene chlorides instead of dimethoxymethane are observed. This fact suggests dimethoxymethane as an intermediate in the CH_2Cl_2 formation probably via the following step.

$$CH_3OCH_2OCH_3 + 4HCl \longrightarrow CH_2Cl_2 + 2CH_3Cl + 2H_2O \qquad (6)$$

Such compound can result from consecutive reactions of methyl formate

$$HCOOCH_3 + CH_2O + H_2O \longrightarrow 2CH_3OH + CO_2 \qquad (7)$$

$$2CH_3OH + CH_2O \longrightarrow CH_3OCH_2OCH_3 + H_2O \qquad (8)$$

Table 2
Products distribution after adsorption of CH_2O and 1 hour reaction with HCl at 373 K

Catalyst	CH_2O adsorption	$CH_2O + HCl$
HY	CO, H_2O, CH_3OH, CH_3OCH_3, trioxan	CO, H_2O, CH_3Cl, CH_3OCH_3, trioxan
NH_4Y	CO_2, H_2O, $HCOOCH_3$, $CH_3OCH_2OCH_3$, trioxan	CO_2, H_2O, CH_3Cl, $HCOOCH_3$, CH_2Cl_2 ClCN, trioxan.

Methyl chloride is the main product in chlorination of CH_2O independently of the cation present in zeolite. In all cases, but NH_4Y, the gas mixtures contain dimethyl other or after CH_2O adsorption such species and methanol were identified. Methanol and metoxy species could be intermediates in the CH_3Cl production. Over alkali metal zeolites methanol could arise from the Cannizzaro reaction (reaction (4)), or subsequent reactions of methyl formate (reaction (7)). A study on the identification of all reaction indermediates and their exact role in the chlorination mechanism is underway.

4. Conclusions

From our findings it is evident that the chlorination of CH_2O with HCl into methylene chloride is not a simple conversion in which acid sites of a catalyst are the only centers involved. On these sites, the intermediates that arised from adsorption of CH_2O are converted into methyl chloride. We believe that methanol or methoxy group-containing species are the potential intermediates responsible for CH_3Cl formation. The key role in the reaction studied seems to play the adsorption step of CH_2O.

Dimethoxymethane formed during CH_2O adsorption on NH_4Y is suggested as an intermediate in CH_2Cl_2 formation. However, the activity of this particular catalyst is only temporary since it gets transformed into the hydrogen form.

Acknowledgment

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

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