

THE CATALYTIC DECOMPOSITION OF FORMIC ACID ON SOME MOLECULAR SIEVES $\text{Na}_{1-x}\text{H}_x\text{Z}$

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On $\text{Na}_{1-x}\text{H}_x\text{Z}$ formic acid is decomposed into $\text{H}_2 + \text{CO}_2$ and $\text{H}_2\text{O} + \text{CO}$. The determination of the reaction mechanisms allows to point out the chemical properties of these solids. Dehydrogenation takes place at high temperature, through the formation of aluminium and sodium formates. Dehydration, which occurs at low temperature, is catalysed by the Brønsted acid sites created during the preparation of the solid or the formation of formates. The strength of this acidity strongly depends on x value.

We have employed the decomposition of formic acid to investigate chemical properties of Z-zeolites in which the parent sodium ions have been partially replaced by H^+ ions. We present our results concerning the overall kinetics of formic acid decomposition and the chemisorption of this molecule as revealed by infrared spectroscopy.

Experimental part

Sample preparation

The cation exchanged zeolites were prepared from Norton sodium Z-type zeolite by treatment with an aqueous solution of nitrate containing various quantities of ammonium ion. $\text{Na}_{1-x}\text{H}_x\text{Z}$ is obtained by decomposition of $\text{Na}_{1-x}\text{NH}_x\text{Z}$. The extent of exchange is given in Table I. Before any experiment the samples were treated at 673 K either in the decomposition vessel or in the IR cell.

Kinetic experiments

Nitrogen, used as the carrier gas, at atmospheric pressure, passes successively through the saturator containing the reactant, the reaction vessel, the traps necessary for the elimination of excess acid and of the water formed, and the IR system for analysis of the carbon monoxide and dioxide formed during the reaction. 10 mg of catalyst are used; the saturator is maintained at 298 K; in this case the amount of formic acid carried over ($11 \cdot 10^{-4}$ moles min^{-1}) is enough to cover completely the catalyst surface, at least at low decomposition rate. The temperature of the reaction vessel is increased from 373 to 573 K in 10 K steps, and the reaction yield is measured when the system is at equilibrium.

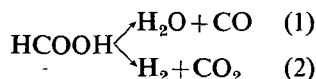
IR Spectroscopy experiments

Formic acid is adsorbed at room temperature on a pellet of the catalyst placed in the IR cell. The acid is desorbed under vacuum at different temperatures increasing from 373 to 573 K. The IR spectrum is recorded on a Perkin Elmer 125 or 225 spectrometer, the sample after each desorption being at the temperature of the IR beam (333 K).

Results and discussion

Determination of the kinetic parameters

We have plotted for each catalyst the variations of $\ln [\text{CO}]$ and $\ln [\text{CO}_2]$ for reactions:



as a function of $\frac{1}{T}$ (Fig. 1). We note first of all that it is often possible to trace these curves by increasing or decreasing the temperature. This shows that these reactions do not poison the active sites of the solids. The kinetic study shows that whatever is

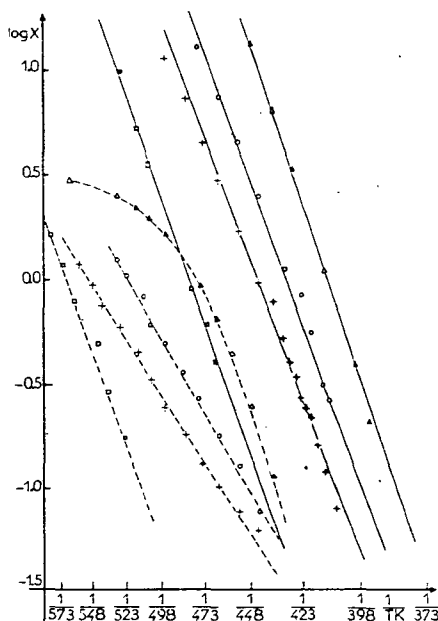


Fig. 1. Arrhenius plots of rate constants for $X = \text{CO}$ (—), $X = \text{CO}_2$ (---) for various values of x : $x = 1$ or 0.5 (Δ), 0.2 (\circ), 0.025 ($+$), 0 . (\square)

the exchange, at low temperature, the decomposition is only a dehydration reaction. Its starting temperature depends on the degree of exchange. For $x \geq 0.5$ all the Arrhenius plots coincide (Fig. 1). But for $x < 0.5$, the greater the extent of decationization, the lower the temperature at which the dehydration reaction starts. To obtain the same amount of CO, the Table I shows that the reaction temperature must be increased monotonically with x , from about 393 K for $\text{Na}_{0.5}\text{H}_{0.5}\text{Z}$ to 453 K for NaZ . In all cases, over a temperature range of about 60 K, $\ln [\text{CO}]$ varies linearly with $\frac{1}{T}$. For all the samples studied the apparent activation energy lies between 20 and 24 kcal mol⁻¹. At higher temperature, the previous straight lines begin to curve owing to a decrease in the coverage of the active sites under the applied experimental conditions or as a consequence of reaction (2).

The case of dehydrogenation is different. Whatever is the value of x ($x = 0$) the reaction always starts at the same tempera-

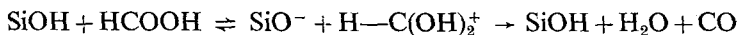
ture 433 K. On NaZ ($x=0$), CO_2 is observed in the gases at 493 K only. As in the case of reaction (1), at higher temperature the Arrhenius plots for all the samples curve toward negative values of $\ln C_{\text{O}_2}$.

IR spectra of chemisorbed formic acid

The IR spectrum of HZ treated at 673 K under vacuum shows the following bands: 3700 cm^{-1} (weak) and 3580 cm^{-1} (strong) characteristic of hydroxyl groups, 1860 and 1620 cm^{-1} due to the lattice. Apart from the 1860 cm^{-1} band, these bands appear during thermal treatment of NH_4Z . The two last ones are found in the other zeolites treated at 673 K under vacuum.

HZ— The IR spectrum of acid adsorbed on HZ at room temperature contains three absorption zones $3500\text{--}3000\text{ cm}^{-1}$, $1700\text{--}1600\text{ cm}^{-1}$ and $1450\text{--}1350\text{ cm}^{-1}$ (Fig. 2). Moreover, the bands at 3700 and 3580 cm^{-1} due to OH groups in the solid are no longer seen because either the O—H bonds are broken or the bands are shifted to low frequencies by strong hydrogen bonding between these OH and the acid molecules. In either case, this result shows that at least part of the adsorbate strongly interacts with the hydroxyl groups of HZ.

Heating at less than 373 K eliminates physically adsorbed acid, which is characterised by an absorption region at about 1700 cm^{-1} . A strong band at 1660 cm^{-1} , typical of strongly interacting $\text{C}=\text{O}$, is then visible. Furthermore, since 393 K is the temperature at which decomposition by reaction (1) begins, it can be deduced that the 1660 and 1400 cm^{-1} bands are attributable to an intermediate stage of the dehydration reaction. The mechanism of this reaction is therefore analogous to that postulated for homogeneous acid media:



The 1660 cm^{-1} band could be associated with either a $\text{C}=\text{O}$ band of an acid molecule in strong interaction with the acid OH groups of the solid, or the antisymmetrical vibration of the $-\text{C} \begin{matrix} \text{OH} \\ \diagup \\ \text{OH} \end{matrix}$ group. We cannot therefore say whether $\text{H}-\text{C}(\text{OH})_2^+$ is stabilised in the Z-zeolites.

The bands 1610 , 1405 and 1385 cm^{-1} which remain in the spectrum after sample desorption at 393 K characterize the aluminum formate formed on the Lewis acid

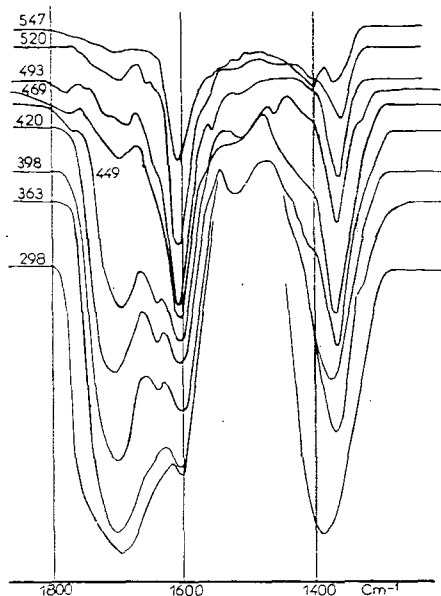
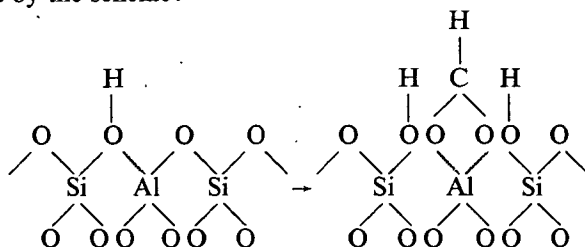


Fig. 2. Infra-red spectra of HCOOH adsorption-desorption on HZ-zeolite

sites of the solid by the scheme:



Compared with the spectrum of aluminum formate [1] we have attributed the bands 1610 and 1385 cm^{-1} to the asymmetric (ν_{as}) and symmetric (ν_s) OCO-stretching vibrations and the 1420 cm^{-1} one to the OCO and CH deformation vibration.

The frequencies ν_{as} and ν_s are both higher than the corresponding ones in ionic formate HCOO^- (1590 and 1350 cm^{-1} respectively). We deduce that the superficial formate is bidentate and involves a covalent bonding with an aluminum atom.

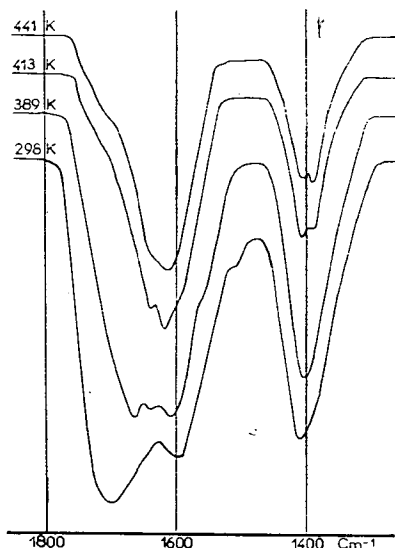


Fig. 3. Infra-red spectra of HCOOH adsorption-desorption on NaZ -zeolite

NaZ— The adsorption of formic acid on NaZ at 300 K leads to the appearance of three bands at 1720 , 1605 and 1400 cm^{-1} . The last one contains at least two badly resolved maxima. The second band and the third, partially, can be attributed to sodium formate during the adsorption and which decomposes at about 493 K . This temperature corresponds to the onset of reaction (2) on this solid; we therefore deduce that this formate ion is an intermediate in this dehydrogenation reaction. Formation of this sodium formate implies the release of a proton which must attach itself to an atom adjacent to aluminium and creates an hydroxyl group analogous to those existing on HZ .

The 1720 cm^{-1} band is associated with the $\text{C}=\text{O}$ band of a chemisorbed acid molecule corresponding to an intermediate of reaction (1) since this reaction begins at the temperature at which this band disappears (448 K). But the position of this band shows that the $\text{C}=\text{O}$ bond interacts rather weakly with the OH groups of the solid. This could explain why it is necessary to have a higher temperature than in other cases in order to form HCOOH_2^+ which is required for dehydration of the acid.

$\text{Na}_{0.5}\text{H}_{0.5}\text{Z}$ — We should point out that the spectra for this catalyst contain only the bands for acid adsorbed on HZ , to the exclusion of those detected in the case of NaZ . This proves that the Na^+ cations situated in the small channels of diameter 2.3 \AA which link two large channels do not take part in the reaction. This is due to the fact that the HCOOH molecule cannot penetrate into those small channels.

The reactivity of zeolites containing 50% of Na^+ cations therefore owes nothing to the sodium. It is therefore easy to understand why HZ and $\text{Na}_{0.5}\text{H}_{0.5}\text{Z}$ have the same activity if it is assumed that for the same reasons the OH groups situated in the small channels of HZ do not constitute active sites.

Variations of the Brönsted acidity strength with the sodium concentration

We have just seen that the dehydration activity of $\text{Na}_{1-x}\text{H}_x\text{Z}$ zeolites depends greatly on the extent of cation exchange. Now the mechanism of this dehydration involves only the capture of a proton of the superficial OH groups by a molecule of acid. We must therefore conclude that the ease of HCOOH_2^+ formation depends on x value. Two explanations are then possible.

(a) the OH groups of the solid, created during the preparation or the formate formation can interact more or less strongly with the formate, depending on its proximity.

(b) the intrinsic acidity of the superficial OH groups would depend on the nature and the concentration of the cations inside the zeolite. This second hypothesis seems the most plausible for the following reasons.

Table I

Catalysts	1	2	3
HZ	393 K	8	13.98
$\text{Na}_{0.5}\text{H}_{0.5}\text{Z}$	393 K	8	13.98
$\text{Na}_{0.8}\text{H}_{0.2}\text{Z}$	403 K	5.4	6.67
$\text{Na}_{0.9}\text{H}_{0.1}\text{Z}$	410 K	4.8	5.69
$\text{Na}_{0.975}\text{H}_{0.025}\text{Z}$	413 K	4.2	4.20
NaZ	453 K	4	0.40

1 — Experiment temperature $[\text{CO}] = 2.68 \cdot 10^{-3}$ mole $\text{g}^{-1}\text{h}^{-1}$

2 — Total number of Brönsted acid sites per unit cell

3 — $T = 423$ K: Turnover number (mole $(\text{H}^+)^{-1}\text{h}^{-1}$)

We calculated for each value of x the number of Brönsted acid sites per unit cell due to the OH arising from the preparation of the solid and to those coming for the formation of formates on the surface (Table I). We deduced the activity reported to one acid site (Table I). We notice that it is increasing with x . For instance when x increases from 0.2 to 0.5, the turnover number is multiplied by 20.

Conclusion

We have been able to determine the mechanisms of formic acid decomposition on $\text{Na}_{1-x}\text{H}_x$ zeolites. The dehydrogenation reaction occurs at low temperature *via* the aluminium formate ($x \neq 0$) and at high temperature through the sodium formate acting as an intermediate ($x < 0.5$).

Dehydration, which occurs at relatively low temperature, is catalysed by the Brönsted acid sites, OH groups created during preparation of the solid or when the formates are formed.

We have demonstrated that the acid strength of these OH groups depends on the Na—H exchange rate and, consequently, that it is possible to create surfaces with very different Brönsted acidities.

References

- [1] *Donaldson, J. D., J. F. Knifton, J. F. Ross: Spectrochimica Acta 20, 847 (1964).*