In situ FTIR study of the kinetics of formic acid decomposition on V–Ti oxide catalyst under stationary and non-stationary conditions. Determination of kinetic constants

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ABSTRACT

Decomposition of formic acid over V–Ti oxide catalyst under stationary and non-stationary conditions was studied by *in situ* IR spectroscopy at temperature range 50–150 °C. The kinetic scheme was shown to include the steps of reverse adsorption of formic acid and formate decomposition to CO. The rate constants and activation energies were estimated according to the proposed kinetic model. The kinetic model satisfactorily describes the experimental data under stationary and non-stationary conditions.
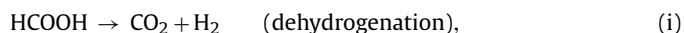
1. Introduction

Formic acid is the main product of formaldehyde oxidation over vanadia–titania (V–Ti–O) catalyst [1]. The selectivity for formic acid attains 95–90%, with formaldehyde conversion varying in the range of 20–90% at 100–130 °C. A narrow range of temperatures providing selective oxidation of formaldehyde is caused by successive decomposition of formic acid that occurs at raising the reaction temperature [1].

Formic acid is a frequently observed intermediate product of the oxidation of organic wastes in both gas and aqueous phases. Hence, it is important to understand the kinetics and mechanism of formic acid decomposition.

Decomposition of formic acid, the simplest carboxylic acid, is a classic reaction in heterogeneous catalysis. It is generally agreed that the reaction network consists of two parallel pathways:

$$HCOOH \rightarrow CO_2 + H_2 \quad \text{(dehydrogenation)}, \quad \text{(i)}$$

$$HCOOH \rightarrow CO + H_2O \quad \text{(dehydration)}. \quad \text{(ii)}$$

The selectivity of formic acid decomposition is used for characterizing the acid–base properties of oxide catalysts: dehydration takes place on acid oxides and dehydrogenation occurs on basic ones [2].

In both dehydrogenation (i) and dehydration (ii) reactions, an adsorbed formate anion ($HCOO^-$) is an important intermediate [3–11]. The rate-determining step during formic acid oxidation is the decomposition of the surface formate intermediate [11,12].

On V–Ti–O catalyst, HCOOH decomposes with a noticeable rate at temperatures above 130 °C. The main pathway is its dehydration (ii) leading to CO and H_2O. In the 20–90% range of HCOOH conversion the selectivity for CO is 90–95%. Other products of HCOOH decomposition are water and CO_2 [13].

The mechanism of formic acid decomposition over V–Ti–O catalyst was studied by *in situ* IR spectroscopy in Ref. [13]. At 50 °C the HCOOH adsorption is accompanied by the formation of hydrogen-bonded HCOOH (ν_{COO^-} at 1715 cm^{-1}) as well as monodentate (ν_{asCOO^-} at 1660 cm^{-1}) and bidentate (ν_{asCOO^-} at 1570 cm^{-1}) formate ions. Increasing the temperature to 100 °C leads to the disappearance of hydrogen-bonded complex HCOOH and decreases the concentration of monodentate formate. In the temperature range 100–200 °C, the main surface compound is bidentate formate ion (BF) (ν_{asCOO^-} at 1556–1570 cm^{-1}).

In the present work, kinetic parameters of the formic acid decomposition over V–Ti–O catalyst are calculated from the data of *in situ* FTIR studies performed under stationary and non-stationary conditions.

2. Experimental

Vanadia–titania catalyst (wt.%) $20V_2O_5–80TiO_2$ (anatase) was prepared by spraying titanium dioxide (anatase) suspension in

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an aqueous vanadyl oxalate solution followed by calcining the obtained powder in air at 450 °C [1]. The surface area of V–Ti–O catalyst is 26 m^2/g.

In situ FTIR spectroscopic measurements were carried out using a flow IR cell-reactor with a Bomem MB-102 FTIR spectrometer. FTIR spectra were collected in transmission mode. The apparatus design and experimental procedures allowed both gaseous products and adsorbed species to be identified under the real conditions. The experiments were conducted at 50–190 °C. For the *in situ* FTIR studies, a flow-through quartz high-temperature IR cell-reactor with the CaF$_2$ windows was used. A catalyst pellet (1 cm × 3 cm in size and ca. 50 mg in weight) was mounted in the flow IR cell-reactor and then pretreated in a flow of air (the volume flow rate V = 50 cm^3/min) at 300 °C for 60 min. All feed pipelines were thermostated at 120 °C.

FTIR spectra of the surface species were recorded at passing the reaction mixture of 1% HCOOH in air at 50–190 °C through the IR cell-reactor with loaded catalyst. The formic acid was dosed until the intensity of infrared bands at a specified temperature became invariant. After establishing a stationary covering with the surface complexes, a 1% HCOOH/air gas mixture was replaced with the air or helium flow, and then the desorption kinetics of surface complexes was studied.

The gas phase was analyzed spectroscopically using a gas IR-cell connected consecutively with the catalytic IR cell-reactor. The changes in the concentrations of surface complexes and gas phase components were determined in parallel experiments.

The concentrations C of the gas products were determined by the Lambert–Bouguer–Beer equation:

$$C\,(\text{mol/l}) = \frac{D}{\varepsilon \times l}, \tag{1}$$

where D is the optical density of the gas mixture, ε is the extinction coefficient, and l is the cell length (cm).

The bands at ν(C–O) = 1105 cm^{-1} corresponding to formic acid were chosen to determine the molecular extinction coefficients ε(C–O) = 46.4 ± 2.0 l/mol cm.

3. Results and discussion

Fig. 1 represents the evolution of FTIR spectra of surface species during desorption in air flow at 100 °C. The bands at 1560 (ν_{asCOO^-}), 1380 (δ_{CH}), 1370 (ν_{sCOO^-}) cm^{-1} indicate the formation of bidentate formate. The bands at 1668 cm^{-1} attributed to ν_{asCOO^-} mode of monodentate formate of are also observed. The weak band at
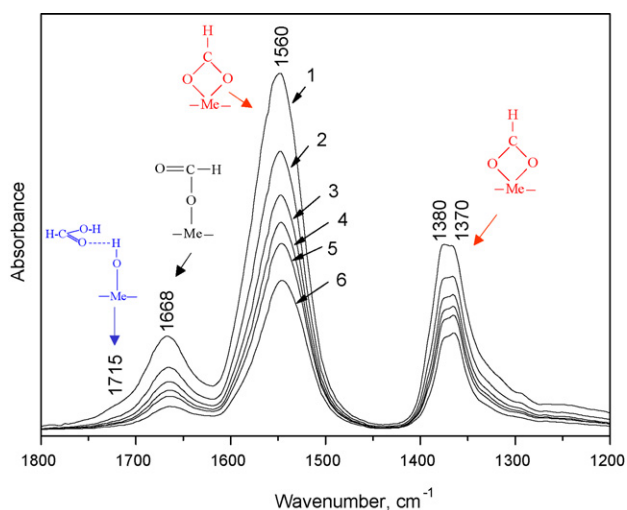

Fig. 1. Evolution of FTIR spectra of surface species during desorption in air flow at 100 °C: 1–0 s, 2–80 s, 3–130 s, 4–180 s, 5–240 s and 6–300 s.
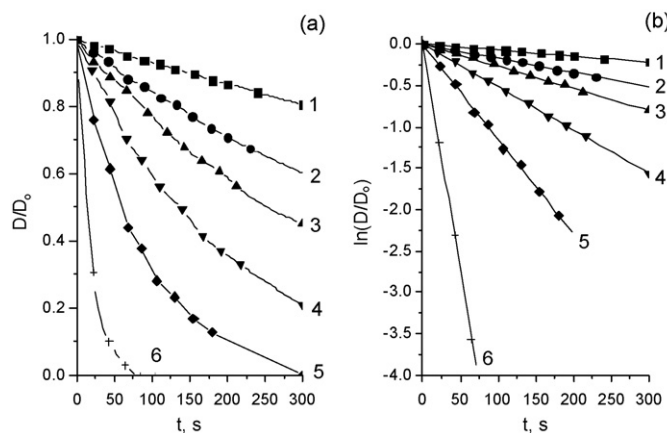

Fig. 2. Time dependences of the relative intensity of the absorption band. ν_{asCOO} of bidentate formates during their changes in air flow in coordinates D/D_o (a) and $\ln(D/D_o)$ (b) at different temperatures: 50 (1), 75 (2), 100 (3), 125 (4), 132 (5) and 150 °C (6).

1715 cm^{-1} ($\nu_{C=O}$) indicates the formation of molecular adsorbed HCOOH [13]. The intensity of all bands is gradually decreased during desorption.

In the investigated temperature range, covering bidentate formate (BF) composes more than 80% relative to the total forms of absorbed formic acid. BF was shown to transform in CO [13].

Fig. 2 shows the experimental data for optical densities D/D_o of the absorption band maximum of bidentate formate ions (ν_{asCOO-}) during their decomposition in air flow at 50–150 °C and the time dependences of $\ln(D/D_o)$ according to [13]. D_o is optical density at steady state conditions.

As follows from the plots in Fig. 2b, the time dependence of $\ln(D/D_o)$ has a linear form at all the temperatures.

Since the relative densities of intensity of the D/D_o band correspond to the catalyst coverage with bidentate formates θ_A, time variation of θ_A can be described by the first order equation:

$$\frac{d\theta_A}{dt} = -k\theta_A,$$

where k is the rate constant. Zero time reference corresponds to the moment when feeding of formic acid to the reactor inlet is stopped. The initial coverage is equal to the stationary value established by this time: at t = 0 the coverage is $\theta_A = \theta_A^0$.

Solution of this equation is of the form $\theta_A = \theta_A^0 \exp\{-kt\}$. Hence it follows a linear dependence on time:

$$\ln\left(\frac{\theta_A}{\theta_A^0}\right) = -kt, \tag{2}$$

Linear regression was used to estimate the constants at different temperatures from experimental data shown in Fig. 2b (Table 1).

Fig. 3 shows the logarithm of constant k for the rate of bidentate formates transformation against the inverse temperature. This dependence takes the form of a broken line. Assuming that the temperature dependence of constant k is described by Arrhenius equation, one can estimate the activation energies for different linear segments. Linear regression gives the following values of apparent activation energy for two temperature ranges: at 50–125 °C E = 6.5 ± 0.4 kcal/mol, whereas at 125–150 °C E = 31.3 ± 1.4 kcal/mol.

In Ref. [14] the mechanism of formaldehyde oxidation on the surface of V$_2$O$_5$–TiO$_2$ catalyst was studied within the density functional theory. According to the suggested mechanism, surface formates are the intermediates of formaldehyde oxidation. Two reaction pathways of formates conversion are considered. The first pathway leads to the formation of adsorbed formic acid

Table 1
Values of constant k (s^{-1}) and confidence intervals Δk at different temperatures.

Parameter	T, °C					
	50	75	100	125	132	150
k	0.00072	0.00170	0.00267	0.00523	0.01145	0.05551
Δk	$\pm 5.59 \times 10^{-6}$	$\pm 1.62 \times 10^{-5}$	$\pm 2.66 \times 10^{-5}$	$\pm 4.32 \times 10^{-5}$	$\pm 1.50 \times 10^{-4}$	$\pm 1.05 \times 10^{-3}$

with zero activation energy due to the protonation of formate. The second pathway leading to the deep oxidation starts by the hydrogen transfer from the HCOO$^-$ group to the terminal oxygen V–OH:HCOO–V–OH $\rightarrow$ COO–V–OH$_2$. Since this pathway is accompanied by breaking the C–H bond, one can expect that its activation energy will be high.

The above data together with the obtained values of activation energy give ground to suggest that low temperatures are favorable mainly for the recombination of bidentate formates with protons and formation of formic acid followed by its desorption at the rate $R_D = k_D \theta_A$, whereas higher temperatures provide the decomposition of bidentate formates at the rate $R_R = k_R \theta_A$. The total rate of changing the concentration of bidentate formates, R_T, is determined by the sum of rates:

$$R_T = R_D + R_R = (k_D + k_R)\theta_A.$$

In this case,

$$k = k_D + k_R = k_{0D} \exp\left(-\frac{E_D}{RT}\right) + k_{0R} \exp\left(-\frac{E_R}{RT}\right).$$

Knowing the values of the sum of constants at different temperatures (Table 1), it is necessary to find the values of k_{0D}, k_{0R}, E_D, and E_R.

Minimization of the target function:

$$Q = \sum_{i=1}^{N} (q_i^{tab} - q_i^{calc})^2,$$

where $q^{tab} = \ln k$, $q^{calc} = \ln\{k_{0D} \exp(-E_D/RT) + k_{0R} \exp(-E_R/RT)$, and $N = 6$, allowed us to estimate pre-exponential factors and activation energies from the data of Table 1 using the Levenberg–Marquardt method:

$$E_D = 5.0 \, \text{kcal/mol}, \qquad E_R = 39.3 \, \text{kcal/mol}.$$

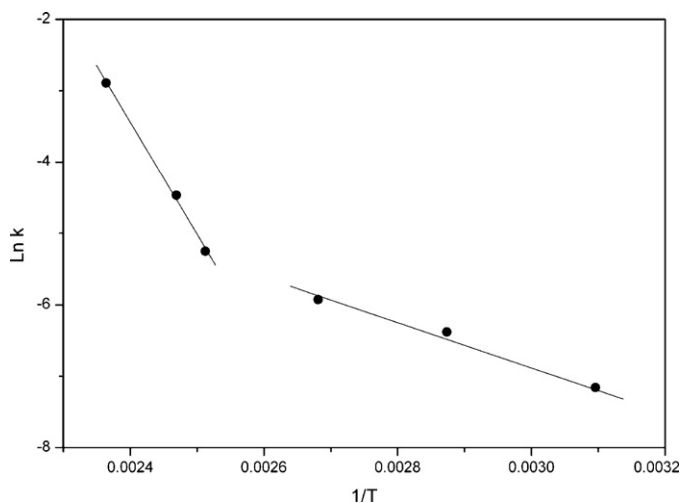The values obtained for linear segments (Fig. 3) were used as the initial estimates for minimization.

Fig. 4 presents the values of $q^{tab} = \ln k$ from Table 1 and the calculated curve $q^{calc} = \ln\{k_{0D} \exp(-E_D/RT) + k_{0R} \exp(-E_R/RT)$ with the obtained parameters (solid line) against the inverse temperature.

The *in situ* FTIR experiment was carried out under stationary conditions using a flow cell-reactor [13]. The initial concentration of formic acid in air or helium was 1%. Table 2 lists the concentrations of formic acid c_A (%) at the cell-reactor outlet at different temperatures.

As seen from Table 2, the presence of oxygen in the feed mixture does not have a pronounced effect on the formic acid decomposition.

When the perfect mixing model is used to describe stationary occurrence of the reaction, balance equations for the concentration of acid in the gas phase and active sites on the catalyst surface can be presented as follows:

$$0 = (c_A^0 - c_A) + \tau[-k_A c_A (1 - \theta_A) + k_D \theta_A], \tag{3}$$

$$0 = k_A c_A (1 - \theta_A) - k_D \theta_A - k_R \theta_A, \tag{4}$$

where $c_A^0 = 0.01$ is the initial concentration of formic acid, c_A is the final concentration of formic acid [mole fractions], $\tau = GZ_T/v = 0.193$ is the conventional contact time [s], v is the reaction mixture molar flow [mol/s], G is the catalyst weight [g], and Z_T is the mole amount of active sites in a gram of catalyst [mol/g].

The fraction of active sites θ_A occupied by bidentate formates is determined from Eq. (4):

$$\theta_A = \frac{k_A c_A}{k_A c_A + k_D + k_R}; \tag{5}$$

the substitution of this expression to Eq. (3) gives the equation:

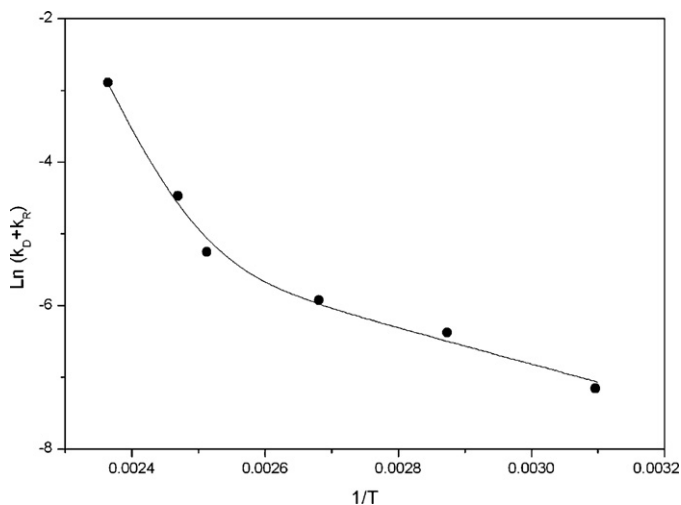$$(c_A^0 - c_A) - \tau\left(\frac{k_A c_A k_R}{k_A c_A + k_D + k_R}\right) = 0,$$

Fig. 3. The logarithm of constant k against the inverse temperature.

Fig. 4. The values of $\ln(k)$ from Table 1 (dots) and the calculated curve $\ln(k_D + k_R)$ (solid line) against the inverse temperature.

Table 2
Stationary concentrations of formic acid at different temperatures.

	T, °C								
	100	120	125	130	132	140	150	160	170
$c_{A\,air}$, %	1.0	0.959	0.940	0.919	0.900	0.750	0.630	0.388	0.247
$c_{A\,He}$, %	1.0	0.956	–	–	–	0.802	0.596	0.427	–

which can be solved with respect to c_A by choosing the branch of positive solutions.

$$c_A = 0.5 \left[-b + \sqrt{b^2 + 4c_A^0 (k_D + k_R)\frac{1}{k_A}} \right], \qquad (6)$$

where $b = \tau k_R - c_A^0 + (k_D + k_R)/k_A$ and $k_A = k_{0A} \exp(-E_A/RT)$.

Non-linear regression applied to the data of Table 2 and the function for c_A from Eq. (6) gives the estimates of parameters k_{0A} и E_A:

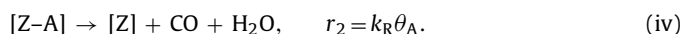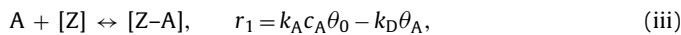$$k_{0A} = \exp(17.38 \pm 4.79), \qquad E_A = (6507.68 \pm 2034.25)R.$$

With the appropriate values of gas constant R, this leads to

$$E_A = 12.9\,\text{kcal/mol}.$$

For comparison, Fig. 5 shows the experimental data (dots) and the calculated curve of stationary values of concentration (Eq. (6)) against the inverse temperature at the obtained constants.

The obtained estimates of kinetic constants can be used to calculate by Eq. (5) the fraction of active sites occupied by bidentate formates against the inverse temperature for the stationary values of θ_A. The calculation results are presented in Fig. 6.

As a result, we have come to the kinetic model that comprises a minimal number of steps and describes quite well the available experimental data.

$$A + [Z] \leftrightarrow [Z\text{–}A], \qquad r_1 = k_A c_A \theta_0 - k_D \theta_A, \qquad (iii)$$

$$[Z\text{–}A] \rightarrow [Z] + CO + H_2O, \qquad r_2 = k_R \theta_A. \qquad (iv)$$

The first step includes the interaction of formic acid from the gas phase (A) with active sites on the catalyst surface [Z] leading to the formation of bidentate formates [Z–A] on these sites, while the reverse step includes the recombination of bidentate formate ions with protons yielding formic acid (A) followed by its desorption to the gas phase; the next step consists in decomposition of bidentate formates accompanied by evolution of carbon monoxide and water.
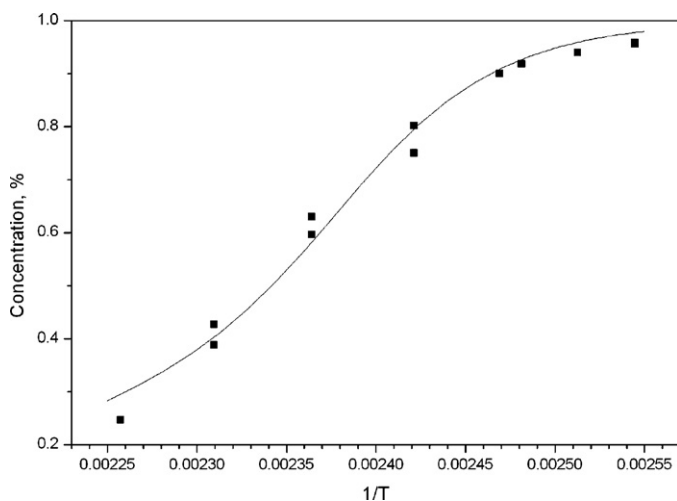

Fig. 5. Experimental data (dots) and calculated curve of stationary values of the formic acid concentration against the inverse temperature.
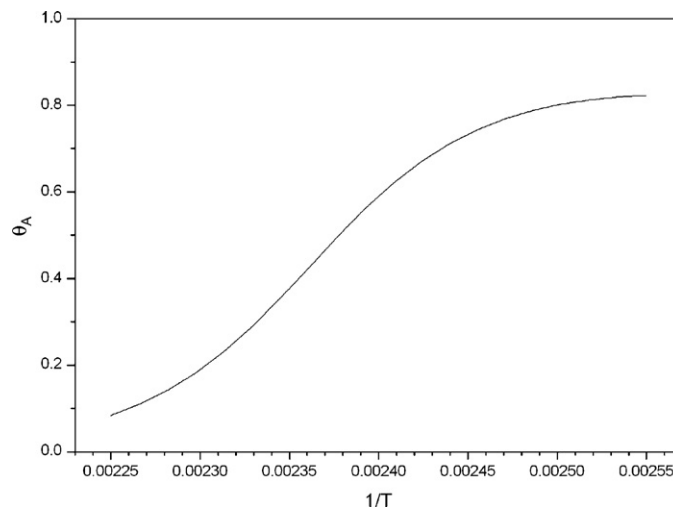

Fig. 6. The calculated curve showing the fraction of active sites occupied by bidentate formates against the inverse temperature under stationary conditions.

Table 3
Estimated kinetic parameters.

k_i, 1/s	E_i, kcal/mol
$k_{0A} = \exp(17.38)$	$E_A = 12.9$
$k_{0D} = \exp(0.72)$	$E_D = 5.0$
$k_{0R} = \exp(43.83)$	$E_R = 39.3$

The kinetic parameters listed in Table 3 make it possible to describe the experimental data obtained both under stationary and non-stationary conditions.

4. Conclusion

Decomposition of formic acid over V–Ti oxide catalyst under stationary and non-stationary conditions was studied by *in situ* IR spectroscopy under temperature range 50–150 °C. The kinetic scheme was shown to include steps of reverse adsorption of formic acid and formate decomposition to CO. The rate constants and activation energies were estimated according the proposed kinetic model. The obtained estimates of kinetic constants were used to calculate the fraction of active sites occupied by bidentate formates for the catalyst stationary state at different temperatures. The kinetic model satisfactorily describes the experimental data under stationary and non-stationary conditions.

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