

# Transient response study of the formaldehyde oxidation to formic acid on V–Ti–O catalyst: FTIR and pulse study

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## Abstract

The mechanism of the formaldehyde oxidation to formic acid on a V–Ti–O catalyst has been studied by pulse and spectrokinetic (in situ FTIR) methods. Bidentate symmetrical formates and asymmetric formates are observed by formaldehyde adsorption both in the presence and in the absence of dioxygen in the temperature range between 100 and 200 °C. Formic acid may form by two parallel pathways: by an associative mechanism through the oxidative elimination of bidentate formates and by a stepwise redox Mars–van Krevelen mechanism through the decomposition of asymmetric formates; the associative mechanism seems to be preferable.

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## 1. Introduction

Formic acid is produced commercially by three methods: carbonylation of methanol to methyl formate followed by hydrolysis, liquid-phase oxidation of *n*-butane or naphtha yielding formic acid as a co-product with acetic acid, and acidolysis of formate salts with sulfuric acid to give sodium sulfate as a by-product. Heterogeneous catalytic oxidation of formaldehyde in the gas phase over vanadia–titania catalyst may be considered as an alternative to multistep liquid-phase syntheses of formic acid [1]. Unlike the liquid-phase processes, direct oxidation of formaldehyde to formic acid is simple to operate and produces no side products, harmful wastewater and off-gas effluents [2].

The feasibility of selective heterogeneous oxidation of formaldehyde to formic acid on oxide catalysts was first demonstrated by Ai. Testing a large number of oxide catalysts in formaldehyde oxidation showed that an enhanced yield of formic acid is obtained with V<sub>2</sub>O<sub>5</sub>-based catalysts. According to Ai, a maximum yield of formic acid was attained with the V–Ti oxide catalyst (atomic ratio 90/10) at the reaction temperature 200 °C and amounted to 19 mol% HCOOH at total conversion of HCHO 36.1 mol% [3]. As reported in Refs. [1,2], in the case

of formaldehyde oxidation on the V–Ti–O catalyst (20% wt V<sub>2</sub>O<sub>5</sub> and 80% wt TiO<sub>2</sub> anatase) in the temperature range of 120–130 °C, the yield of formic acid was ca. 85% (at formaldehyde conversion 90% and selectivity to formic acid 95%).

The mechanism of formaldehyde selective oxidation to formic acid has received little attention in the literature; however, many studies are devoted to elucidating the nature of surface compounds that form upon interaction of formaldehyde with oxide, in particular V–Ti–O catalysts [4–11].

Busca et al. [4], studying the formaldehyde adsorption on various oxides (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, MgO, ZrO<sub>2</sub>, ThO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>) in the temperature range of 170–570 K, proposed a scheme of HCHO transformation at the surface of metal oxides. According to this scheme, at up to or below room temperature formaldehyde polymerizes on the surface of oxide catalysts to form polyoxymethylene compounds (POM), which further transform into dioxymethylene compounds (DOM). DOM may also form from the coordinately bound formaldehyde, with nucleophilic sites of oxides being involved in the process. Heating up to or above room temperature results in the disproportionation of DOM into formate and methoxide group via Cannizzaro-type mechanism. Formate ions also form by a parallel route, involving direct oxidation of DOM and coordinated formaldehyde.

The surface compounds formed during the interaction between formaldehyde and the vanadia catalysts supported on

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TiO<sub>2</sub> have been studied by FTIR method in [5–11]. Upon adsorption of formaldehyde at room temperature, two surface species were observed, namely, molecularly chemisorbed formaldehyde and DOM. These species are oxidized to formate ions easily by heating. The same formate ions were observed by the authors of [5–11] upon interaction of methanol with vanadia–titania catalyst. The direction of formate transformation during methanol oxidation over V–Ti–O catalysts depends on the temperature and composition of the reaction mixture. At temperatures above 180 °C formates decompose, releasing CO to the gas phase. However, when methanol is present in the gas mixture, the esterification of surface formate ions occurs already at room temperature, and the formation of methyl formate proceeds faster than its decomposition to CO. The reaction of surface formate groups with water yields formic acid.

The surface compounds formed during the interaction between formaldehyde and the vanadia–titania catalyst (20% V<sub>2</sub>O<sub>5</sub>–80% TiO<sub>2</sub> anatase) has been studied by in situ FTIR method in [12–14]. Two types of formates, bidentate symmetrical formates (BF) and asymmetric formates (AF), are produced during selective oxidation of formaldehyde on the V–Ti–O catalyst,  $S_{\text{BET}} = 26 \text{ m}^2/\text{g}$  [12]. Only the BF formates form on the surface of the V–Ti–O catalyst,  $S_{\text{BET}} = 139 \text{ m}^2/\text{g}$  [13,14].

In the present work, transient response the pulse technique and in situ FTIR spectroscopy were used to investigate the mechanism of oxygen involvement in the formation of formic acid.

## 2. Experimental

### 2.1. Catalysts

Vanadia–titania catalyst (wt%) 20V<sub>2</sub>O<sub>5</sub>–80TiO<sub>2</sub> (anatase) was prepared by spraying titanium dioxide (anatase) suspension in 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<sup>2</sup>/g.

There are two forms of vanadium in the catalyst, namely, the V<sub>2</sub>O<sub>5</sub> phase and the octahedral vanadium species strongly bound to TiO<sub>2</sub> [15].

### 2.2. Transient response study of the formaldehyde oxidation

The pulse kinetic studies were performed in a pulse setup with a fluidized-bed catalyst at atmospheric pressure. Stationary state of the catalyst was established via pulse injection of the reaction mixture (2% CH<sub>2</sub>O in air) onto the catalyst pretreated in flowing air at 300 °C for 1 h. The catalyst reduction was carried out with pulses of the reducing mixture (2% CH<sub>2</sub>O in He) onto a freshly pretreated catalyst. The rates of the catalytic reaction and the catalyst reduction with formaldehyde were measured under the steady state in separate pulses of the reaction or reducing mixtures, respectively. The time between pulses depended on the duration of chromatographic analysis and was equal to 5 min. The gas-chromatographic analysis of the reaction products was performed with a thermal conductivity detector and columns filled either with Porapak T (the detection of CH<sub>2</sub>O, HCOOH, HCOOCH<sub>3</sub>, and H<sub>2</sub>O) or a CaA molecular sieve (CO, O<sub>2</sub>, N<sub>2</sub>).

A Fourier IR spectrometer BOMEM MB-102 (Canada) was used to study the mechanism of the formaldehyde oxidation. For the in situ FTIR studies, a flow-through quartz high-temperature IR cell-reactor with the CaF<sub>2</sub> windows was employed [16]. A catalyst pellet (1 cm × 3 cm in size and ca. 50 mg in weight) was placed in the flow IR cell-reactor and then pretreated in air flow (the volume flow rate  $V = 50 \text{ cm}^3/\text{min}$ ) at 300 °C for 60 min. All feed pipelines were thermostated at 120 °C. Gaseous formaldehyde is generated by heating a paraformaldehyde at 90 °C. The weight fraction of formaldehyde in paraform was 95.1%, water being the balance. Formaldehyde vapors were entrained by the flow of air or He passing over the paraform layer. Before feeding formaldehyde to the reactor, water was preliminary blown off from paraform.

The spectral transient response studies were carried out by changing over the composition of the gas flow as follows: air → CH<sub>2</sub>O/air → CH<sub>2</sub>O/He → CH<sub>2</sub>O/air → He → air. 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:

$$C \text{ (mol/l)} = \frac{D}{\epsilon l} \quad (1)$$

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

The bands at  $\nu(\text{CO}) = 2110 \text{ cm}^{-1}$  of carbon monoxide,  $\nu(\text{C}=\text{O}) = 1744 \text{ cm}^{-1}$  of formaldehyde, and  $\nu(\text{C}-\text{O}) = 1105 \text{ cm}^{-1}$  of formic acid were chosen to determine the molecular extinction coefficients ( $\epsilon$ ).  $\epsilon(\text{CO}) = 5.4 \pm 0.2 \text{ l/mol cm}$ ,  $\epsilon(\text{C}=\text{O}) = 27.5 \pm 1.5 \text{ l/mol cm}$ ,  $\epsilon(\text{C}-\text{O}) = 46.4 \pm 2.0 \text{ l/mol cm}$ .

The concentrations  $N$  of surface formates were determined by the formula:

$$N \text{ (molecules/m}^2\text{)} = \frac{D}{\epsilon l}$$

where  $D$  is the optical density of the absorption bands  $\nu_{\text{as}}(\text{COO}^-)$  related to the surface formates, and  $l = \rho S_{\text{sp}}$  is the pellet “thickness”. Here  $\rho$  is the ratio of the pellet mass (g) to the pellet cross-section area (cm<sup>2</sup>), and  $S_{\text{sp}}$  is the BET specific surface area of the catalyst (m<sup>2</sup>/g).  $\epsilon(\nu_{\text{as}}(\text{COO}^-)) = 5 \times 10^{-19} \text{ cm}^2/\text{molecules}$  [16].

The specific rates  $r$  of the reaction products formation at the formaldehyde oxidation were calculated by equation for a differential reactor:  $r \text{ (molecules/m}^2 \text{ s)} = \frac{VCX \times 10^{-2} \times 6.03 \times 10^{23}}{22.4gS_{\text{sp}}}$  where  $V$  is the flow rate (l/s, normal condition) of the reaction mixture,  $C$  the initial concentration of CH<sub>2</sub>O (mol/l),  $X$  the conversion of CH<sub>2</sub>O (%),  $g$  is the catalyst weight (g).

The decomposition rates  $r_d$  of the surface species were calculated in assumption of the first order reactions by equation:

$$r_d \text{ (molecules/m}^3 \text{ s)} = kN$$

where  $k$  is the rate constant (s<sup>-1</sup>) determined from kinetic desorption curves, which were treated satisfactorily in the coordinates of the first order reaction [17].

### 3. Results and discussion

Formic acid is the main product of the formaldehyde oxidation over V–Ti–O catalysts. The selectivity to formic acid was 98–93% at 120 °C over the range of formaldehyde conversion from 10% to 80%. CO and methyl formate are formed in minor amounts [1,2].

#### 3.1. Pulse studies of the formaldehyde oxidation

Oxygen can be involved in the formation of oxidation products over oxide catalysts by two mechanisms: stepwise redox and associative [18]. To estimate the relative contribution of each mechanism at the formaldehyde oxidation on the V–Ti–O catalyst, it is necessary to compare the rates and selectivities of product formation in the catalytic reaction and upon catalyst reduction by formaldehyde.

Fig. 1a and b shows changes in the conversion of formaldehyde (X), the selectivity to formic acid (HCOOH), carbon monoxide (CO) and methyl formate (MF) (a), and their formation rates (b) versus the number of pulses of the 2% CH<sub>2</sub>O/air mixture while the catalyst reaches its stationary state. Establishment of the stationary state is accompanied by an increase in the rate of formic acid formation and a decrease in the rate of CO formation. Methyl formate appears among the reaction products only at the sixth pulse. Selectivities to the reaction products follow the changes in the rates of particular reactions.

An abrupt decrease in the formic acid formation rate and conversion is observed after pulse injection of the reducing mixture (2% CH<sub>2</sub>O/He) onto the catalyst that reached its stationary state. The rates of the CO and methyl formate formation vary negligibly. The reversion from the CH<sub>2</sub>O/He pulse to the CH<sub>2</sub>O/air one restores the stationary values of conversion, rate and selectivity to formic acid.

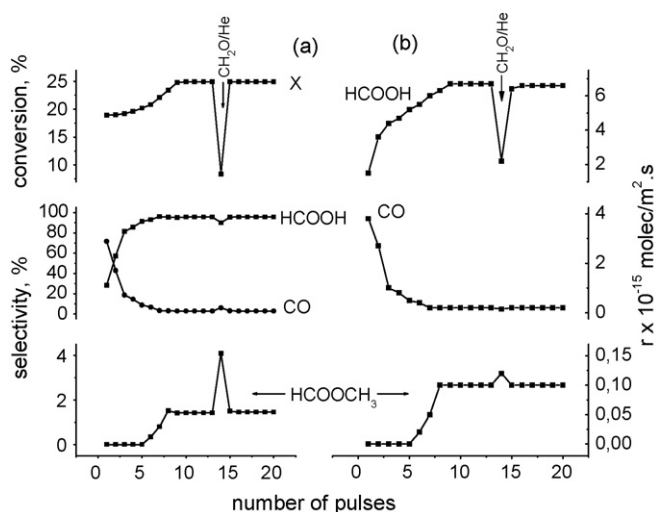


Fig. 1. The dependence of (a) the conversion of formaldehyde (X), the selectivities to formic acid (HCOOH), carbon monoxide (CO) and methyl formate (HCOOCH<sub>3</sub>) and (b) of the rates of formic acid (HCOOH), carbon monoxide (CO) and methyl formate (HCOOCH<sub>3</sub>) formation over V–Ti–O catalyst at 120 °C vs. the number of pulses of the mixtures CH<sub>2</sub>O/air.

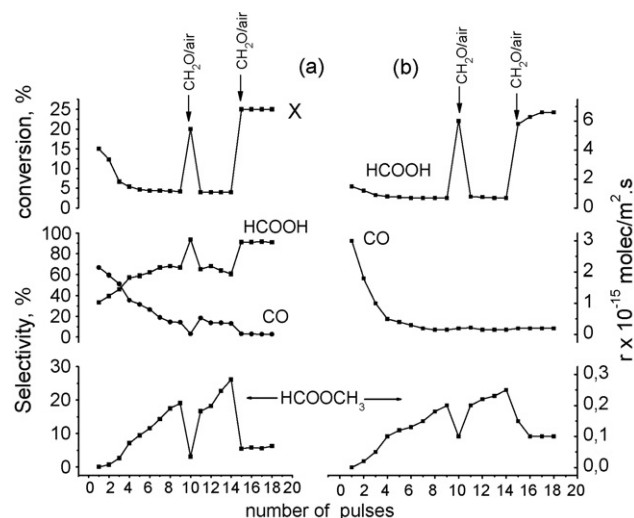


Fig. 2. Changing of (a) the conversion of formaldehyde (X), the selectivities to formic acid (HCOOH), carbon monoxide (CO) and methyl formate (HCOOCH<sub>3</sub>) and (b) of the rates of formic acid (HCOOH), carbon monoxide (CO) and methyl formate (HCOOCH<sub>3</sub>) formation over V–Ti–O catalyst at 120 °C vs. the number of pulses of CH<sub>2</sub>O/He → CH<sub>2</sub>O/air → CH<sub>2</sub>O/He → CH<sub>2</sub>O/air.

Fig. 2a and b shows evolution of the conversion of formaldehyde (X), the selectivity to formic acid (HCOOH), carbon monoxide (CO) and methyl formate (MF) (a), and their formation rates (b) that occurred when the pulse composition was changed as follows: CH<sub>2</sub>O/He (9 pulses) → CH<sub>2</sub>O/air (1 pulse) → CH<sub>2</sub>O/He (3 pulses) → CH<sub>2</sub>O/air (4 pulses).

If fresh catalyst is treated by the CH<sub>2</sub>O/He pulses, a decrease in formaldehyde conversion and rates of the CO and formic acid formation is observed. The rate of the methyl formate formation increases with increasing the number of CH<sub>2</sub>O/He pulses. The injection of CH<sub>2</sub>O/air pulse after reduction pulses sharply increases the conversion, formation rate and selectivity to formic acid. The rate of the CO formation varies negligibly, the rate of methyl formate formation decreases. The reversion from CH<sub>2</sub>O/air pulse to CH<sub>2</sub>O/He leads again to an abrupt decrease in the conversion, formation rate and selectivity to formic acid. When the CH<sub>2</sub>O/air pulses are changed over to CH<sub>2</sub>O/He ones, the formaldehyde conversion, selectivity and rate of formic acid formation attain their stationary values.

As seen from Figs. 1b and 2b, the rate of the formic acid formation is nearly 3.5 times higher in the oxygen-containing pulses (CH<sub>2</sub>O/air) as compared to the CH<sub>2</sub>O/He pulses, which are free of oxygen. These results indicate the formation of formic acid via the associative mechanism involving the gas phase oxygen. The rates of the CO formation in the presence and in the absence of oxygen are close to each other, which points to the Mars–van Krevelen redox mechanism.

#### 3.2. In situ FTIR studies

Fig. 3 shows the FTIR spectra acquired at 120 °C when the reaction mixture of composition 2% CH<sub>2</sub>O/He (A) or 2% CH<sub>2</sub>O/air (B) is passed through the IR cell-reactor loaded with the V–Ti–O catalyst. Two types of formates, bidentate symmetrical formates (BF) and asymmetric formates (AF), form upon

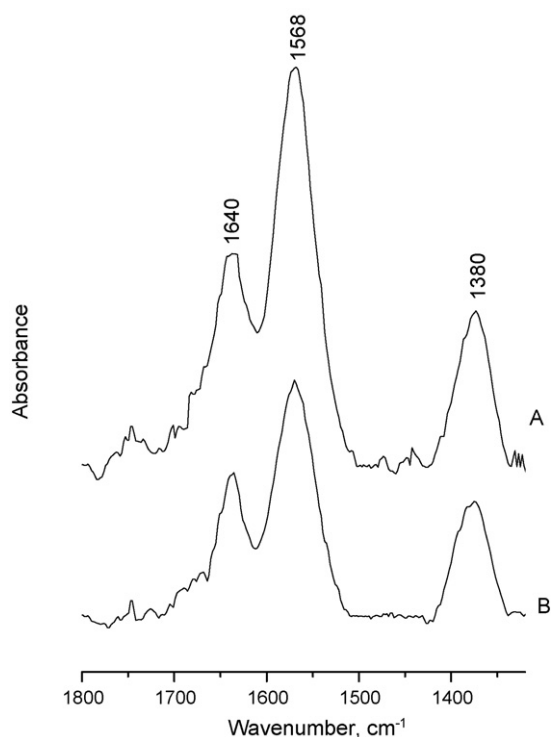


Fig. 3. FTIR spectra for the formaldehyde adsorption on V–Ti–O at 120 °C in the flow CH<sub>2</sub>O/He (A) and CH<sub>2</sub>O/air (B). Spectrum obtained by subtraction the spectrum of the original catalyst from the spectrum obtained after CH<sub>2</sub>O adsorption.

the interaction of formaldehyde with the catalyst. Absorption bands (a.b.) at 1568 and 1380 cm<sup>-1</sup> characterize  $\nu_{as}(\text{COO}^-)$  and  $\nu_s(\text{COO}^-)$ , respectively, in bidentate symmetrical formates (BF) [19]. a.b. at 1640 cm<sup>-1</sup> characterize  $\nu_{as}(\text{COO}^-)$  in a surface

formate with an asymmetric coordination of the COO<sup>-</sup> group (AF) [19]. Since the same surface formates form upon formaldehyde adsorption in the presence and in the absence of oxygen in the reaction mixture, this suggests that the catalyst oxygen is involved in the formaldehyde oxidation to formate ions.

Fig. 4a and b shows evolution of the concentration of the gas mixture components CH<sub>2</sub>O, HCOOH, CO and surface BF and AF formates versus the time of passing the gas flow of different composition through the cell-reactor loaded with the V–Ti–O catalyst. The gas composition was changed over as follows: air → CH<sub>2</sub>O/air → CH<sub>2</sub>O/He → CH<sub>2</sub>O/air (Fig. 4a) and then CH<sub>2</sub>O/air → He → air (Fig. 4b).

Surface BF and AF form immediately after substituting the CH<sub>2</sub>O/air reaction mixture for the air flow, which passes through the cell-reactor loaded with the catalyst. The formate coverages BF, AF and concentrations of formaldehyde (CH<sub>2</sub>O) and formic acid (HCOOH) increase for 15 min after feeding the reaction mixture and then vary negligibly.

Note that a considerable amount of CO is detected among the gaseous products of the reaction at the initial moment after feeding the mixture. Presumably, CO forms due to the interaction between CH<sub>2</sub>O and weakly bound oxygen of the catalyst, which exists on the catalyst surface at the initial moment. The CO concentration decreases to zero in ca. 2 min.

When the CH<sub>2</sub>O/air flow is changed over to CH<sub>2</sub>O/He, the concentration of formaldehyde increases and that of formic acid decreases (Fig. 4a). In the process, the surface concentration of BF increases and that of AF varies negligibly. The reversion to the CH<sub>2</sub>O/air mixture restores the former level of all concentrations and coverages.

When helium is substituted for the CH<sub>2</sub>O/air mixture (Fig. 4b), this is accompanied by removal of gaseous CH<sub>2</sub>O and HCOOH, and by minor changes in the BF and AF coverage.

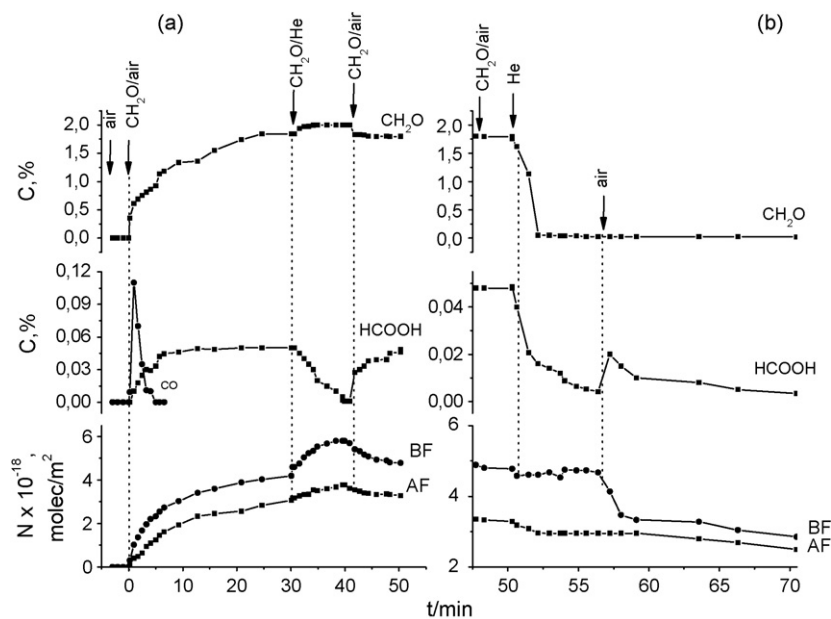
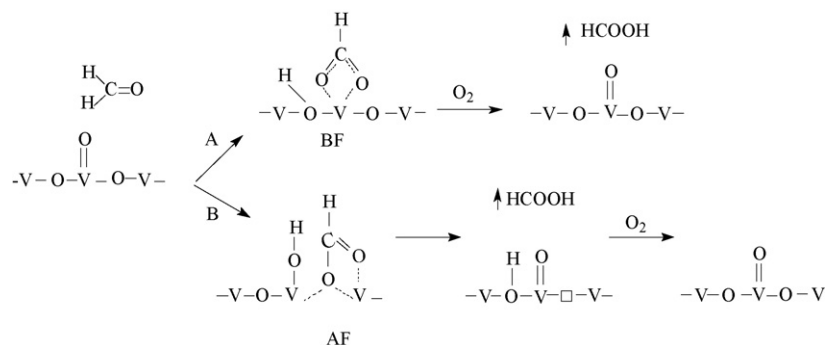


Fig. 4. Changing of the concentration of formaldehyde (CH<sub>2</sub>O), formic acid (HCOOH), carbon monoxide (CO) in gas phase and the catalyst coverage with bidentate symmetrical formates (BF) and asymmetric formates (AF) after step changes of the composition of the reaction mixture CH<sub>2</sub>O/air → CH<sub>2</sub>O/He → CH<sub>2</sub>O/air (a) and CH<sub>2</sub>O/air → He → air (b) over catalyst V–Ti–O catalyst at 120 °C.



Scheme 1. Mechanism of the formaldehyde oxidation to formic acid on V–Ti–O catalyst. (A) The associative mechanism and (B) Mars–van Krevelen mechanism.

Table 1

The rate  $r_d$  of the surface compounds disappearance and the rate  $r$  of the formic acid formation on the V–Ti–O catalyst in the He flow

$T$ (°C)	$N$ ( $\times 10^{-18}$ molecules/m <sup>2</sup> )		$r_d$ ( $\times 10^{-15}$ molecules/m <sup>2</sup> s)		$r$ ( $\times 10^{-15}$ molecules/m <sup>2</sup> s), HCOOH
	BF	AF	BF	AF	
100	3.0	–	0.1	–	–
120	3.3	2.4	0.3	0.3	0.3
130	3.6	3.0	0.6	0.7	0.7

The substitution of He for air results in an abrupt decrease in the BF coverage and an increase in the concentration of formic acid. A further decrease in the formic acid concentration is symbate with the decrease in BF concentration (Fig. 4b).

It is seen that BF formate coverage and concentration of HCOOH in the gas phase depend on the presence of dioxygen in the reaction mixture. The AF coverages are virtually equal in the presence and in the absence of oxygen.

Tables 1 and 2 compare the rates of the BF and AF disappearance ( $r_d$ ) and the rates of the formic acid formation ( $r$ ) in He (Table 1) and in the presence of dioxygen (Table 2) at 100, 120 and 130 °C.

The rates of the AF decomposition are equal in He and air flows. The rate of the formic acid formation in He flow is equal to the rate of the AF decomposition (Table 1). BF decompose much more slowly in He than in the air flow (Tables 1 and 2). At 100 °C, when the AF coverage is small, the rate of the formic acid formation is close to the rate of the BF decomposition in air (Table 2). At 120 and 130 °C the rate of the formic acid formation is closely to the sum of BF and AF decomposition rates in the presence of oxygen and exceeds by an order of magnitude the rate of the formic acid formation in He flow (Tables 1 and 2).

Table 2

The rate  $r_d$  of the surface compounds disappearance and the rate  $r$  of the formic acid formation on the V–Ti–O catalyst in the air flow

$T$ (°C)	$N$ ( $\times 10^{-18}$ molecules/m <sup>2</sup> )		$r_d$ ( $\times 10^{-15}$ molecules/m <sup>2</sup> s)		$r$ ( $\times 10^{-15}$ molecules/m <sup>2</sup> s), HCOOH
	BF	AF	BF	AF	
100	3.0	–	3.1	–	2.9
120	3.3	2.4	5.0	0.4	5.1
130	3.6	3.0	6.2	0.7	6.7

Therefore, results of the pulse and in situ FTIR studies indicate two parallel pathways of the formic acid formation at the formaldehyde oxidation on V–Ti–O catalyst: formic acid forms by the associative mechanism upon decomposition of the surface bidentate formates and by a stepwise redox Mars–van Krevelen mechanism through the decomposition of asymmetric formates. These mechanisms can be represented by a simplified Scheme 1.

#### 4. Conclusion

Bidentate symmetrical formates and asymmetric formates are observed by formaldehyde adsorption on V–Ti oxide catalyst both in the presence and in the absence of dioxygen on V–Ti oxide catalyst. Formic acid may form by two parallel pathways: by an associative mechanism through the oxidative elimination of bidentate formates and by a stepwise redox Mars–van Krevelen mechanism through the decomposition of asymmetric formates. The associative mechanism seems to be preferable.

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