

# Determination of surface intermediates during the selective oxidation of formaldehyde over V–Ti–O catalyst by in situ FTIR spectroscopy

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## Abstract

Formaldehyde oxidation to formic acid on V–Ti–O catalyst was studied in a flow-circuit setup with a differential reactor and in the IR cell. Surface intermediates leading to formic acid formation were identified. Catalyst calcination temperature was varied to study its effect on catalyst performance and surface species structure. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* V–Ti–O catalyst; Formaldehyde; Surface intermediates; IR spectroscopy

## 1. Introduction

V–Ti–O catalysts were found to be selective in formaldehyde oxidation to formic acid [1]. In the present communication, we discuss surface intermediates generated during formaldehyde oxidation on the V–Ti–O catalyst, and catalyst calcination temperature effect on the structure and transformation of these surface species.

## 2. Experimental

V–Ti–oxide catalyst (20% V<sub>2</sub>O<sub>5</sub>–80% TiO<sub>2</sub>) was prepared by mixing vanadium oxalate solutions with titanium dioxide, followed by drying and calcination at 300°C (VTi300), 400°C (VTi400) and 450°C (VTi450) in air for 4 h [2].

Catalyst performance was studied in a flow-circuit setup with differential reactor under atmospheric pressure at 120°C.

In situ FTIR spectroscopy experiments were done using a differential flow IR cell-reactor with Bomem BM-102 FTIR spectrometer allowing adsorbed species analysis under reaction conditions. Experiments were performed at 20–200°C using 2.2 vol.% CH<sub>2</sub>O in air flow.

## 3. Results and discussion

### 3.1. Catalyst properties

Catalyst properties are listed in Table 1. Samples VTi300 and VTi400 show a higher activity than VTi450. Reaction selectivity towards formic acid does not depend on the temperature of catalyst calcination.

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Table 1  
Catalytic properties of samples V–Ti–O<sup>a</sup>

N/n	S <sub>BET</sub> (m <sup>2</sup> /g)	N (V atoms/nm <sup>2</sup> )	τ, c <sup>b</sup>	Conversion of CH <sub>2</sub> O (%)	Selectivity S <sub>HCOOH</sub> (%)	r 10 <sup>-7</sup> (mol CH <sub>2</sub> O/g c)
VTi300	234	5.7	3.0	66.7	84.0	10.7
VTi400	139	9.5	3.6	69.1	84.3	7.5
VTi450	30	27.6	7.4	65.0	85.0	3.6

<sup>a</sup>Reaction conditions: reaction temperature (°C) = 120, concentrations CH<sub>2</sub>O-6.5–7% in air.

<sup>b</sup>τ-contact time.

Samples VTi300 and VTi400, characterized by a large specific surface, allow the vanadia coverage close to the calculated monolayer (8 V atoms/nm<sup>2</sup>, Ref. [3]). As calcination temperature increases from 300°C to 450°C, the catalyst specific surface decreases dramatically, and the coverage by vanadia becomes postmonolayer. As a result, oxide vanadium species crystallize, and phase V<sub>2</sub>O<sub>5</sub> appears.

### 3.2. In situ FTIR study

Fig. 1 represents the in situ FTIR spectra of catalysts V–Ti–O recorded during formaldehyde oxidation at 70°C and 120°C. Reaction mechanism derived from the FTIR data is schematically shown in Fig. 2. H-bonded HCHO (SS1) ( $\nu(\text{C}=\text{O}) = 1724 \text{ cm}^{-1}$ ), dioxymethylene

complexes (SS2) ( $\delta(\text{CH}_2) = 1478 \text{ cm}^{-1}$  and  $\omega(\text{CH}_2) = 1410 \text{ cm}^{-1}$ ) and symmetric bidentate formate (SS3) ( $\nu_{\text{as}}(\text{COO}) = 1567 \text{ cm}^{-1}$ ,  $\delta(\text{CH}) = 1380 \text{ cm}^{-1}$  and  $\nu_{\text{s}}(\text{COO}) = 1370 \text{ cm}^{-1}$ ) form during formaldehyde adsorption at 70°C on all studied samples. Besides all above described species, sample VTi450 carries asymmetric formate (SS4) ( $\nu_{\text{as}}(\text{COO}) = 1640 \text{ cm}^{-1}$ ) [4].

The bands of the H-bonded HCHO are observed at temperatures below 85°C. As temperature increases to 100°C, the bands of dioxymethylene complexes disappear, while intensity of the bands of bidentate formate increases, and, in addition, the weak bands appear corresponding to methoxy-groups (SS5). Simultaneously with formic acid appearance in the gas phase, IR spectra show absorption band at  $1668 \text{ cm}^{-1}$ , which we ascribe to  $\nu_{\text{as}}(\text{COO})$  in a

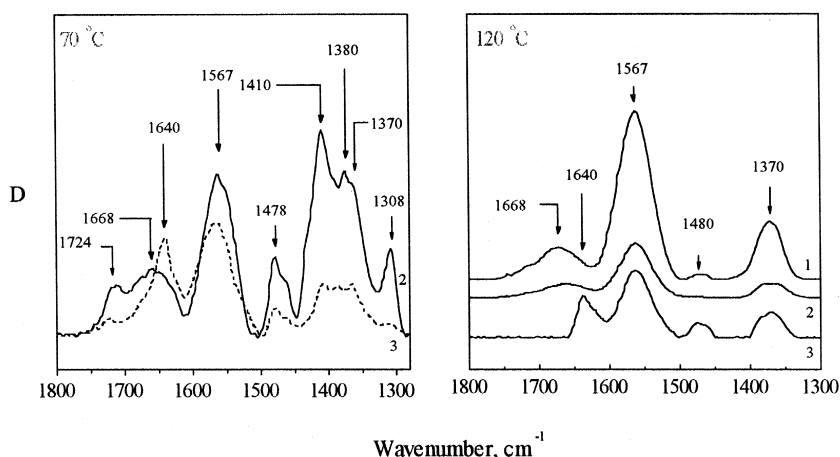


Fig. 1. In situ FTIR differential spectra of 20% V<sub>2</sub>O<sub>5</sub>–80%TiO<sub>2</sub> during formaldehyde oxidation at 70°C and 120°C: (1) VTi300, (2) VTi400 and (3) VTi450.

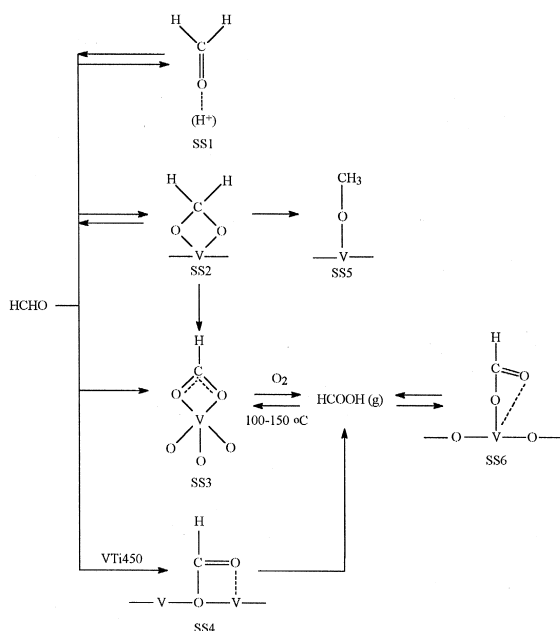


Fig. 2. Reaction scheme of formaldehyde oxidation on V–Ti–O catalyst.

monodentate formate (SS6) [4], the last is the product of formic acid readsorption. This surface species is observed on formic acid adsorption on all studied catalysts.

At temperatures optimum for the formic acid synthesis (100–150°C) on catalysts calcined at 300–400°C, formaldehyde adsorption produces solely symmetric bidentate formate SS3. Symmetric SS3 and asymmetric SS4 formates form on the samples calcined at 450°C (see Fig. 1). Our kinetic and in situ transient FTIR experiments [4,5] have shown symmetric bidentate formate to be of key importance for the formic acid synthesis. This formate is stable up to 180°C on adsorption in helium, but readily decomposes in oxygen presence at 100–150°C yielding formic acid evolution into the gas phase. Activation energy of this decomposition is 28.4 kJ/mol and is very close to the activation energy of formic acid formation (28.8 kJ/mol). Formate SS4 are also destroyed within catalysis temperatures yielding formic acid, but their decomposition rate is by the order of magnitude

lower than that of bidentate formate, and does not depend on the oxygen present.

Quantum chemistry ab initio method MO/HF was used to build the model of active site on the V–Ti–O catalyst and energy profiles for formic acid formation from formates SS3 and SS4. Cluster  $V_2O_5OH_2$  was used as the active site model (Fig 3).

The model active site contains two  $VO_4$  units connected by a bridging V–O–V band. Each  $VO_4$  unit contains single terminal V=O band and one Lewis site. Calculations show that the highly reactive bidentate formates SS3 form, when formaldehyde interacts with vanadyl oxygen (V=O), whereas less reactive formates SS4 are generated, as formaldehyde reacts with bridge oxygen V–O–V.

According to the literature, monomer vanadyls, polyvanadates and crystal  $V_2O_5$  occur on the surface of supported  $V_2O_5$  [6–8]. The ratio between these species is determined by the surface coverage. Most likely, on the samples with large specific surface (VTi300 and VTi400), vanadium species are mainly isolated units  $VO_4$ . When the temperature of catalyst calcination increases, the catalyst specific surface dramatically decreases. On sintering, the isolated species  $VO_4$  decrease in number, whereas polyvanadates and  $V_2O_5$  crystals grow, being characterized by typical bonds V–O–V.

Therefore, the catalyst activity decrease with the growing catalyst calcination temperature is most likely related to the change in the structure of surface vanadium species and their concentration.

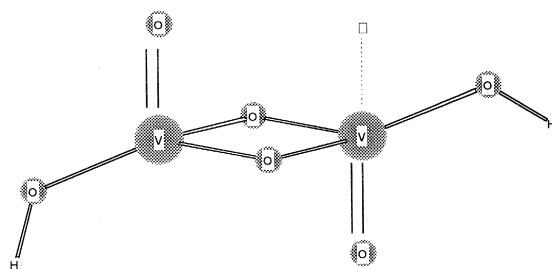


Fig. 3. The model of active site of the V–Ti–O catalyst.

## Acknowledgements

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