

Heterogeneous selective oxidation of formaldehyde to formic acid on V/Ti oxide catalysts: The role of vanadia species

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Abstract

The present work deals with the study of the role of vanadium species in the V/Ti-supported oxide catalysts for the oxidation of formaldehyde to formic acid. Two different series of catalysts were prepared, the first one consisting of catalysts of composition 20 wt.% V_2O_5 /80 wt.% TiO_2 calcined at 400 and 450 °C (series 1), and the second one was prepared by washing of series 1 samples with nitric acid (series 2). All the samples were characterized by XRD, IR spectroscopy, temperature-programmed reduction with H_2 , and differential dissolution methods. In the catalysts of series 1, vanadium is represented by both monolayer species (monomeric and polymeric VO_x) and V_2O_5 phase in crystalline or X-ray amorphous state, depending on the calcination temperature. Washing the samples of series 1 with nitric acid removes the V_2O_5 phase, and the samples of series 2 contain only monolayer vanadium species. The monolayer vanadia–titania catalysts are highly active in the formaldehyde oxidation to formic acid, while crystalline and amorphous V_2O_5 exhibit a low activity in that reaction. Moreover, the presence of the V_2O_5 phase blocks the catalyst active sites and thus decreases the catalyst activity. The monolayer vanadium species are easier to be reduced by H_2 as compared to bulk V_2O_5 . © 2007 Elsevier B.V. All rights reserved.

Keywords: Supported vanadia catalysts; Formaldehyde oxidation; Vanadium species

1. Introduction

Anatase-supported vanadium oxide catalysts (V/Ti) are known to be highly active and selective in oxidation and oxidative ammonolysis of various hydrocarbons [1–5], oxidative dehydrogenation of alkanes [6–9] and reduction of nitrogen oxides [10] and thus are the subject of extensive studies.

A lot of studies on the vanadia–titania systems were aimed at elucidating the nature of their catalytic action and the structure of surface vanadium species and their reactivity [11–34]. The last was the topic of special issues of *Catalysis Today* [24,25]. According to spectroscopic investigations, on the titania support isolated monomeric vanadyl species, polymeric vanadia species and V_2O_5 crystallites are to coexist, their relative abundance being related to the vanadia content. It is well known that crystalline vanadium species predominate on the high-loaded samples, whereas on the low-loaded samples monomeric and

polymeric species predominate, which have strong interaction with the support. The samples which contain monomeric and polymeric vanadium species are commonly referred as “monolayer” samples.

It is known that a treatment (chemical attack) of the high-loaded V/Ti oxide samples with *i*-butanol or aqueous solutions of ammonia and some mineral acids (HNO_3 and H_2SO_4) leads to the dissolution of both the bulk and polymeric vanadium species, the monomeric species being not attacked [1,4,23–26,28,30,31]. According to Refs. [1,24], the amount of insoluble vanadium is commonly less than 0.1–0.4 of the monolayer, whereas by the data of [4,23] it slightly exceeds a monolayer.

The lattice oxygen bond strength is generally considered to be the main parameter, which determines the activity and selectivity of oxide catalysts in the oxidation of hydrocarbons [35]. Some correlations are usually observed between the reducibility of vanadium species and their activity in partial oxidation of hydrocarbons [5,12–14,20,21,28–34]. For example, the experiments on the temperature-programmed reduction (TPR) in hydrogen and oxidation in oxygen (TPO) were performed with the V_2O_5/TiO_2 catalysts with vanadia loadings of

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either 1 wt.% (Eurocat EL10V1) or 8 wt.% (Eurocat EL10V8) [24,25,33]. The monomeric vanadyl species which were present on the Eurocat EL10V1 appeared to be the easiest to reduce but the most difficult to reoxidize [33]. In paper [30], three types of vanadia species were identified on vanadia/titania catalysts with 0.2–2.6 ml of VO_x on the titania surface. Their reducibility in hydrogen was characterized by peak maximum in the TPR profiles indicating isolated monomeric species (≤ 497 – 507°C), polymeric species (537°C), and bulk amorphous V_2O_5 (579°C) [30].

The role of individual vanadium species in selective oxidation of hydrocarbons is not yet fully understood. The monomeric VO_x species are known to form the main active sites for the conversion of isopropanol to acetone [24]. Also, the monomeric VO_x species are more active in oxidative ammonolysis of methyl pyrazine as compared to bulk V_2O_5 [4]. The monolayer vanadium species (both monomeric and polymeric) were shown to be responsible for the catalytic activity and selectivity in respect to benzaldehyde and benzoic acid in partial toluene oxidation over V/Ti oxide catalysts [31,32]. A comparison of samples with different vanadium content in their specific activity in the toluene oxidation indicated that the supported vanadia–titania catalysts appear to be one order of magnitude more active than pure bulk V_2O_5 [31]. The specific activity in the oxidation of toluene and the selectivity in respect to benzaldehyde and benzoic acid exhibited by the supported vanadia–titania catalysts were found to increase with the vanadium loading up to the monolayer coverage [32]. This increase was attributed to the parallel increase of the surface concentration of easily reducible isolated vanadium species interacting with the anatase surface. When the vanadium content increased above monolayer coverage, both activity and selectivity decreased [32].

In the temperature range of 120 – 140°C , the supported vanadia–titania (10–90 wt.% V_2O_5 /90–10 wt.% TiO_2) catalysts were found to exhibit high selectivity in the oxidation of the formaldehyde to formic acid [36]. So, irrespective of the vanadium content, the selectivity in respect to formic acid attains 95–85% in the range of formaldehyde conversion of 35–85% at the reaction temperature of 120°C . On the contrary, the specific activity of the samples depends on the amount of vanadium supported on anatase.

Our work was aimed at identifying the most active vanadium species in supported V/Ti oxide catalysts for the oxidation of formaldehyde to formic acid.

2. Experimental

2.1. Catalyst preparation

The catalysts were synthesized using a commercial TiO_2 (anatase) (catalog Alfa Aesar) with specific surface area of $350\text{ m}^2/\text{g}$. Two series of samples have been prepared.

Series 1. The vanadia–titania oxide catalysts of the composition 20 wt.% V_2O_5 /80 wt.% TiO_2 were prepared by the impregnation of TiO_2 with a water solution of vanadyl oxalate synthesized from V_2O_5 (>99.6%, Reachim, Russia) and oxalic acid (>97%, Reachim, Russia). The samples were dried in air at

110°C for 24 h and calcined in air flow (50 ml/min) at 400°C (VTi400) or 450°C (VTi450) for 4 h.

Series 2. The samples of series 1 were washed with 10% water solution of nitric acid by the method described in Ref. [4] to remove the individual V_2O_5 phase. After washing, the samples VTi400 and VTi450 were calcined once more at 400°C (VTi400w) or 450°C (VTi450w), respectively, for 4 h.

2.2. Physico-chemical properties (techniques)

The specific surface area was calculated by the BET method, from the nitrogen adsorption isotherms obtained by an automated Micromeritics ASAP-2400 apparatus.

Powder XRD diffraction patterns were obtained using a Siemens D500 diffractometer (Germany) with the monochromated $\text{Cu K}\alpha$ radiation.

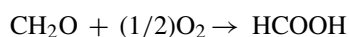
IR spectra were recorded using a FT-IR spectrometer BOMEM MB-102 (Canada). To take the spectra, the samples were pretreated by a standard method, the pelletizing with CsI (2 mg of the sample and 500 mg of CsI).

The chemical composition of compounds formed in the supported catalysts was determined by the differential dissolution (DD) method [37,38]. The DD method consists in dissolving the sample under analysis in an appropriate solvent, the concentration (or chemical potential) of which increases intentionally during the dissolving procedure. The procedure makes it possible to dissolve progressively and selectively the phases, which constitute the analyzed sample and express the kinetic of dissolution as the curves of release of the analyzed chemical elements into the solvent. To find the chemical formulae of these dissolving phases, and their quantities, the original kinetics curves of dissolving elements are transformed into stoichiograms which represent the molar ratios of the element dissolution rates versus time. Such stoichiograms make it possible to derive chemical formulae of the phases under dissolution while the curves of the phase dissolution allow the finding of quantities of these phases. The concentration of dissolved V and Ti in the flow of the solvent was determined by means of ICP atomic emission analyzer (ICP, Baird). H_2O , HCl (1.2 and 3N), and HF (3.8N) were consecutively used as the solvent. The temperature of the solvent was increased gradually from 60 to 80°C .

The temperature-programmed reduction in hydrogen was performed with 100 mg of a 0.25–0.5 mm fraction of catalysts in a quartz reactor using a flow setup with a thermal conductivity detector. Prior to the reduction, the samples were treated in oxygen for 0.5 h at 400°C and then cooled to room temperature in the O_2 atmosphere. The reducing mixture (10 vol.% H_2 in Ar) was fed at the rate of $40\text{ cm}^3/\text{min}$ and the rate of heating from room temperature to 900°C was $10\text{ K}/\text{min}$.

2.3. Catalytic tests

The catalytic properties of the samples were studied in the reaction of the formaldehyde oxidation at 120°C :



The steady-state activity of the catalysts was tested at atmospheric pressure by the differential method at a flow circulation setup [35,39]. The reactor (i.d. 12 mm, length 50 mm) was made of Pyrex glass with a coaxial thermocouple pocket ($d=4$ mm) for temperature measurements in the catalyst bed. The reactor was placed into an electrical oven with the air heating. The temperature was controlled with the accuracy ± 0.5 °C using a temperature controller. To prevent the product condensation, the circulation circuit was thermostated at 120 °C.

The composition of the initial mixture (vol.%) was as follows: 5% CH₂O, 10% H₂O, air balance. Gaseous formaldehyde for the catalytic studies was obtained via thermal decomposition of paraform (“Methyl” Company, Russia). The weight fraction of formaldehyde in paraform was 95.1%, water being the balance. Before feeding formaldehyde to the reactor, water was preliminary blown off from paraform. The formaldehyde was dosed by the flow of air passing over the paraform layer at 100 °C. The water was dosed by the saturation of air stream at a given temperature. The flow and circulation rates of the reaction mixture were 8.2 and 800 l/h, respectively. The catalysts were sieved; in the experiments the fraction from 0.25 to 0.50 mm was used. The concentration of formaldehyde and the reaction products (formic acid, methyl formate and carbon oxides) were determined by chromatography.

The conversion of formaldehyde was calculated by the following equation:

$$X(\%) = \frac{C_{\text{CH}_2\text{O}}^0 - C_{\text{CH}_2\text{O}}}{C_{\text{CH}_2\text{O}}^0} \times 100$$

where $C_{\text{CH}_2\text{O}}^0$ is the inlet concentration of CH₂O, vol.%; $C_{\text{CH}_2\text{O}}$ is the outlet CH₂O concentration, vol.%

The rate of the formaldehyde oxidation (molec. m⁻² s⁻¹) and turn over frequency (TOF, s⁻¹) was expressed as the catalytic activity.

The steady-state rate (r) of the formaldehyde oxidation was calculated by an equation for a differential reaction:

$$r(\text{s}^{-1}) = \frac{F \times C \times 10^{-2} \times X \times 10^{-2} \times 6.03 \times 10^{23}}{22.4 \times g \times S_{\text{BET}}}$$

and

$$\text{TOF}(\text{s}^{-1}) = \frac{r}{N_s \times 10^{18}}$$

where F is the flow rate (l/s, normal condition) of the inlet reaction mixture; C is the inlet concentration of CH₂O (vol.%;); X is the conversion of CH₂O (%); g is the catalyst weight (g); S_{BET} is the specific surface area of catalyst; N_s is the surface vanadium loading ($V_{\text{at}}/\text{nm}^2$). The number of surface vanadium atoms ($V_{\text{at}}/\text{nm}^2$) was calculated with respect to the BET area of catalyst.

The selectivity in respect to HCOOH, CO, CO₂ and HCOOCH₃ was calculated with respect to the transformed molecules of CH₂O to suit the stoichiometric coefficients of individual reactions.

Carbon balance was at least $97 \pm 2\%$ for all experiments.

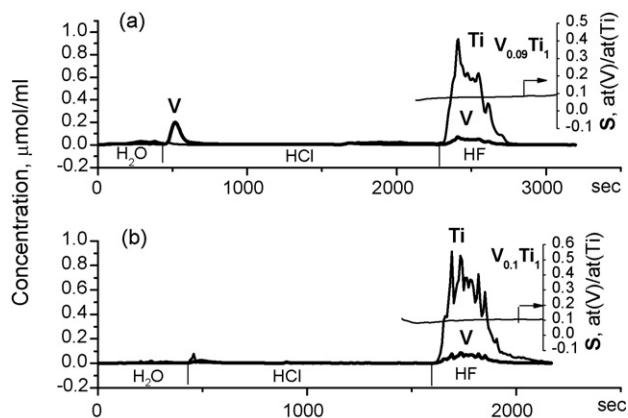


Fig. 1. Kinetic dissolution curves of vanadium (V) and titanium (Ti) and corresponding stoichiograms ($S, \text{at.V/at.Ti}$) for the VTi400 (a) and VTi400w (b) samples.

3. Results and discussion

3.1. Physico-chemical characteristics of the catalysts

Figs. 1 and 2 show the kinetic dissolution curves and stoichiograms (V:Ti) for VTi400 and VTi400w (Fig. 1a and b) and VTi450 and VTi450w (Fig. 2a and b) samples.

Two vanadium species, those with either weak or strong bonding to TiO₂, can be identified in the samples of the initial composition of 20 wt.% V₂O₅/80 wt.% TiO₂ after its calcination at 400 and 450 °C (Figs. 1a and 2a). The weakly bonded vanadium is dissolving in a diluted hydrochloric acid as an individual vanadium compound without an admixture of titanium. The strongly bonded vanadium is dissolved in hydrofluoric acid simultaneously with titanium. Stoichiograms in Figs. 1 and 2 (figures, insets) characterize the ratio of vanadium and titanium concentrations in the solvent versus the degree of the sample dissolution. A section of the stoichiogram corresponding to the simultaneous dissolution of vanadium and titanium is characterized by the atomic ratio V/Ti=0.083–0.1.

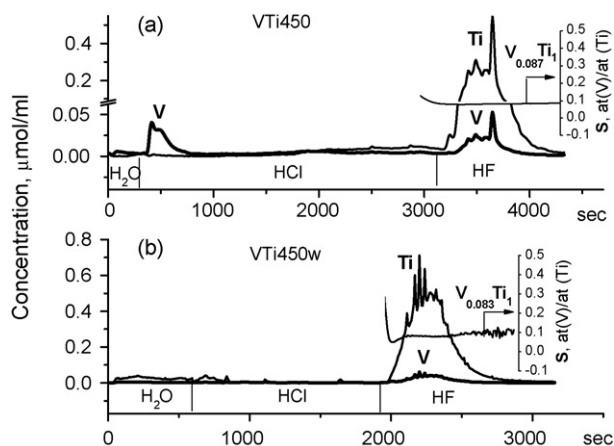


Fig. 2. Kinetic dissolution curves of vanadium (V) and titanium (Ti) and corresponding stoichiograms ($S, \text{at.V/at.Ti}$) for the VTi450 (a) and VTi450w (b) samples.

Table 1
Physico-chemical properties of the samples

No.	Sample	V ₂ O ₅ content (wt.%)	S _{BET} (m ² /g)	^a N _s (Vat/nm ²) ^a	Relative content of vanadium in its species (%)	
					Weakly bonded	Strongly bonded
1	VTi400	20	111	11.9	37.5	62.5
2	VTi400w	12.5	115	7.3	–	100
3	VTi450	20	53	24.4	63.5	36.5
4	VTi450w	7.3	54	8.9	–	100

^a Referred to the BET area of the catalyst.

In the samples of series 2 (VTi400w and VTi450w), nearly all vanadium is represented by the strongly bonded species since washing the samples with nitric acid removes the weakly bonded vanadium (Figs. 1b and 2b).

Table 1 presents the results of the chemical analysis of the series 1 and 2 samples obtained by the differential dissolution method. As is seen from Table 1, at the same overall content of vanadium in the samples of series 1, the relative content of weakly and strongly bonded vanadium species differs. Elevating the calcination temperature from 400 to 450 °C decreases the specific surface area and increases the relative content of weakly bonded vanadium which is represented by V₂O₅ phase.

After the treatment of the series 1 samples with nitric acid, their surface area does not change, whereas the amount of vanadium in the sample decreases. The density of vanadium particles on the surface of the samples of series 2 is 7.3–8.9 VO_x/nm² (Table 1), which is close to the monolayer coverage. The maximum content of vanadium in a dense monolayer on pure anatase, as determined by the Raman spectroscopy [1,11], attains 7–8 VO_x/nm². According to the literature data, the monolayer V/Ti oxide samples contain both monomeric and polymeric VO_x species.

As follows from the XRD and IR spectroscopy data, the weakly bonded vanadium which is dissolving in HCl as an individual the compound is amorphous or crystalline V₂O₅. Fig. 3 shows the diffraction patterns of TiO₂ (anatase) and V/Ti samples of series 1 and 2. The diffraction pattern of the VTi450 sample after the calcination at 450 °C (curve 2) contains not only the reflexes of anatase (curve 1), but also the reflexes of the crystalline V₂O₅ phase. The intensity of reflexes of the crys-

talline V₂O₅ phase is much lower when the sample of the same composition is calcined at 400 rather than at 450 °C (curve 3). This may relate to the fact that a major part of the weakly bonded vanadium oxide before the vanadium washing with nitric acid is in an amorphous state; this conclusion is confirmed by IR spectroscopy (Fig. 4). A wide and strong absorption in the frequency region of 900–250 cm⁻¹ is observed in the IR spectrum of anatase (spectrum 6). The spectra of series 1 catalysts (spectra 2 and 3) contain, in addition to the absorption bands of anatase, the bands assigned to the stretching vibrations of V–O–V (at 960 and 930 cm⁻¹) and V=O (at 1022 cm⁻¹ for VTi450 and at 1011 cm⁻¹ for VTi400) fragments. A broadening of the ν(V=O) band and shifting its absorption maximum to the low-frequency region (from 1022 to 1011 cm⁻¹) for the VTi400 sample relative to the spectrum of bulk V₂O₅ may be caused by a higher dispersity as compared with the VTi450 dispersity of vanadium in this sample. The V₂O₅ bands are absent in the spectra of series 2 samples regardless of the calcination temperature; the diffraction patterns of these samples contain only the reflexes of anatase.

3.2. TPR study of the catalysts

Fig. 5a shows the TPR curves for VTi400 (curve 1) and VTi400w (curve 2). The curve 3 exhibits the difference of these curves. The similar curves for the VTi450 and VTi450w samples are presented in Fig. 5b.

Upon the catalyst reduction, more than one peak of the hydrogen absorption is observed. Thus, these data indicate

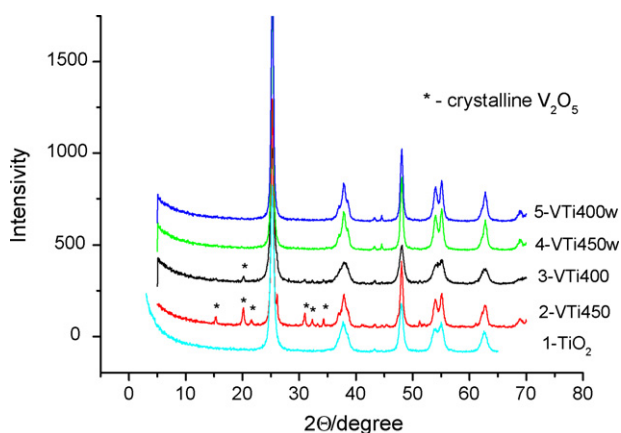


Fig. 3. XRD patterns of TiO₂-anatase (1) and of the V/Ti samples (2–5).

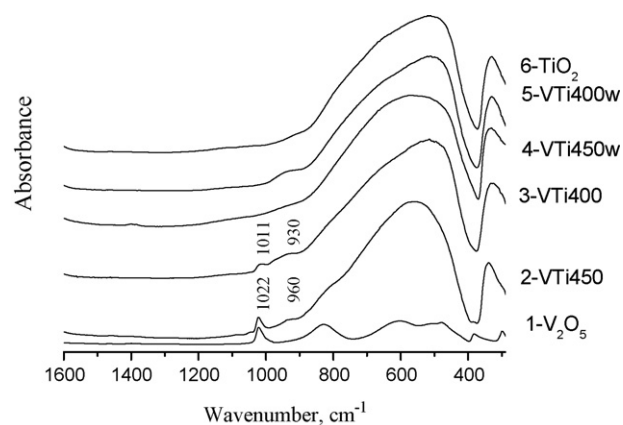


Fig. 4. The FT-IR spectrum of the V₂O₅ (1), V/Ti samples (2–5) and TiO₂-anatase (6).

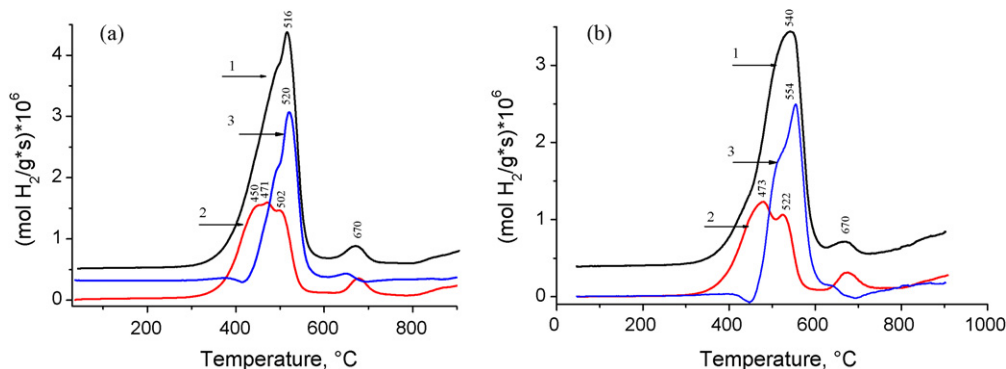


Fig. 5. The TPR profiles of the V/Ti samples before (1) and after (2) treatment in HNO_3 . Curve (3) is the difference curve obtained by subtracting the 1 and 2 curves. (a) VTi400 and VTi400w samples; (b) VTi450 and VTi450w samples.

the presence of several types of oxygen-containing vanadium species on the TiO_2 surface. The low-temperature peaks in the region of 450–502 °C for VTi400w (Fig. 5a, curve 2) and 473–522 °C for VTi450w (Fig. 5b, curve 2) are evidently related to the reduction of the monolayer vanadium species.

The presence of more than one maximum in the TPR curves of VTi400w and VTi450w samples (curve 2), which contain only the strongly bonded vanadium, indicates that insoluble vanadium species are not homogeneous, but contain the monomeric and polymeric VO_x particles. The temperature region at 450–470 °C characterizes the monomeric VO_x species, while the peaks at a higher temperature (502–522 °C) can be attributed to the reduction of polymeric species.

According to the DD and XRD data, washing of the series 1 samples with nitric acid removes the amorphous and crystalline V_2O_5 species weakly bonded to the support. Thus, the temper-

ature maxima in the difference spectra (Fig. 5, curve 3) can be assigned to the V_2O_5 phase which can be removed by the nitric acid. The distinctions in the temperature maxima of the difference reduction curves obtained with VTi400 ($T_{\text{max}} = 520$ °C) and VTi450 ($T_{\text{max}} = 554$ °C) may relate accordingly to the reduction of amorphous and crystalline V_2O_5 .

An easier reduction of monomeric vanadium species, as compared to polymeric and crystalline vanadia, was demonstrated elsewhere [24,25,30,33]. In particular, for sample Eurocats EL10V1 (1% $\text{V}_2\text{O}_5/\text{TiO}_2$, $S = 10 \text{ m}^2/\text{g}$) which contained only the monomeric vanadium species, the TPR curves show a single peak with $T_{\text{max}} = 487$ °C [33]. As it was shown in [30], the insoluble monomeric species are reduced in hydrogen at $T \leq 497$ – 507 °C.

Thus, one can assume that the monolayer vanadium species are characterized by more weakly bonded oxygen as compared to oxygen in the bulk V_2O_5 phase.

Table 2

The catalytic properties of bulk V_2O_5 and the V/Ti catalysts at the reaction temperature of 120 °C

No.	Catalyst	S_{BET} (m^2/g)	V^a (ml)	X^b (%)	Selectivity (%)				r ($\times 10^{16}$ molec./ m^2 s)	TOF ($\times 10^{-3}$ s^{-1})
					HCOOH	HCOOCH ₃	CO	CO ₂		
1	V_2O_5	5.9	5.9	2.6	92.8	6.1	1.1	–	0.23	0.002
2			10.5	6.1	91.8	6.1	2.1	–	0.26	0.002
3			20.5	8.9	94.5	2.0	3.5	–	0.22	0.002
4	VTi400	111	0.3	15.3	96.5	1.5	1.5	0.5	2.06	1.734
5			1.3	35.3	95.8	2.1	1.5	0.6	1.71	1.430
6			1.9	52.5	95.7	1.8	2.0	0.5	1.17	0.980
7			2.9	55.6	95.0	2.0	2.1	0.9	0.82	0.687
8			3.1	66.7	94.9	1.6	2.4	1.1	0.85	0.713
9			6.2	75.2	93.6	1.1	3.2	2.1	0.48	0.402
10			9.3	82.7	90.3	1.2	4.5	4.0	0.35	0.293
11	VTi400w	115	2.3	76.5	93.7	1.3	3.5	1.5	1.60	2.223
12			3.6	84.4	90.8	1.0	5.0	3.2	1.03	1.427
13	VTi450	53	9.8	70.2	94.9	1.6	2.0	1.5	0.59	0.236
14			14.8	78.3	93.5	1.2	3.0	2.3	0.44	0.177
15	VTi450w	54	5.1	78.8	92.8	1.2	3.5	2.5	1.31	1.488
16			6.8	83.1	90.7	1.0	4.8	3.5.0	1.03	1.164

The composition of the initial mixture (vol.%): 5% CH_2O , 10% H_2O , air the balance. The flow rate of the reaction mixture – 8.2 l/h.

^a V is the catalyst volume (the catalyst bulk density 0.6–0.7 g/cm^3).

^b X is the formaldehyde conversion; r is the specific rate of the formaldehyde oxidation.

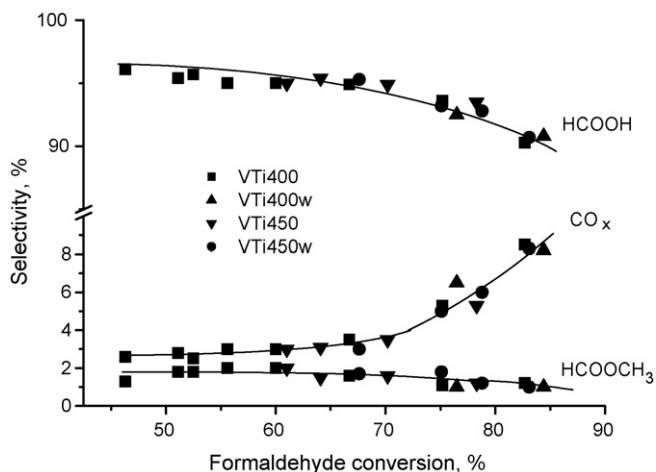


Fig. 6. Selectivities of the supported V/Ti oxide catalysts in respect to formic acid (HCOOH), CO_x ($\text{CO} + \text{CO}_2$) and methyl formate (HCOOCH_3) vs. formaldehyde conversion at 120°C .

3.3. Catalytic properties

The catalytic properties of bulk V_2O_5 and the V/Ti catalysts under study are presented in Table 2.

One can see that the bulk V_2O_5 is low active as compared with the supported V/Ti oxide catalysts. However, bulk V_2O_5 demonstrates high selectivity in the oxidation of formaldehyde to formic acid. The selectivity in respect to formic acid exceeds 90% at the formaldehyde conversion of ca. 10%. The side products of the oxidation are methyl formate and carbon oxides. Deposition of vanadia on TiO_2 increases sharply the rate of formaldehyde oxidation.

Fig. 6 shows the selectivity in respect to the different reaction products versus the formaldehyde conversion for the VTi400, VTi450, VTi400w and VTi450w samples. The selectivities for all VTi samples fit well in the common curves. Evidently, the presence of the V_2O_5 phase in the samples does not deteriorate the selectivity.

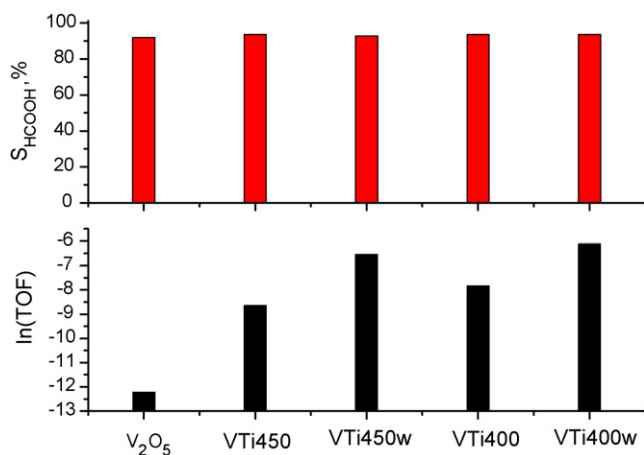


Fig. 7. Comparison of the selectivity to formic acid (S_{HCOOH}) and activity $\ln(\text{TOF})$ for the V_2O_5 and V/Ti oxide catalysts at the temperature of the reaction 120°C . The conversion of formaldehyde is $78 \pm 2\%$ for V/Ti catalysts and 8.9% for V_2O_5 .

Fig. 7 displays the selectivity and activity of the formaldehyde oxidation to formic acid ($\ln(\text{TOF})$) for the supported V/Ti oxide catalysts of series 1 and 2 at the comparable conversion of formaldehyde ($X = 78 \pm 2\%$). The same kinetic characteristics for V_2O_5 are presented at the conversion of formaldehyde of ca. 10%. The activity of the series 2 samples which contain vanadium as monolayer species is higher as compared to similar samples of series 1, which comprise all three vanadium species identified. Selectivity in respect to the formic acid is the same for all the samples.

4. Conclusion

The activity of V/Ti oxide samples is determined by the nature of vanadium oxide species. Strongly bonded to TiO_2 monomeric and polymeric oxygen-containing vanadium species as well as amorphous and crystalline V_2O_5 are present in the samples. The relative content of oxygen-containing vanadium species depends on the amount of vanadium and temperature calcination of the samples.

Therefore, one can conclude that observed increase in the activity of the supported V/Ti oxide catalysts as compared with bulk V_2O_5 is caused by the formation of monolayer vanadium oxide species. The monolayer vanadium–titania catalysts are highly active in the formaldehyde oxidation to formic acid. According to the TPR data, these vanadium species are easier to reduce by H_2 as compared to bulk V_2O_5 .

The bulk V_2O_5 is highly selective, but low active in respect to the oxidation of formaldehyde to formic acid as compared with the supported V/Ti oxide catalysts. The presence of bulk amorphous or crystalline V_2O_5 in the V/Ti oxide catalysts leads to a partial blocking of the active sites and hence decreases the catalyst activity in the oxidation of formaldehyde to formic acid.

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