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Selective oxidation of methanol to form dimethoxymethane and methyl formate over a monolayer V_2O_5/TiO_2 catalyst



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ABSTRACT

The oxidation of methanol over highly dispersed vanadia supported on TiO_2 (anatase) has been investigated using in situ Fourier transform infrared spectroscopy (FTIR), near ambient pressure X-ray photoelectron spectroscopy (NAP XPS), X-ray absorption near-edge structure (XANES), and a temperature-programmed reaction technique. The data were complemented by kinetic measurements collected in a flow reactor. It was found that dimethoxymethane competes with methyl formate at low temperatures, while the production of formaldehyde is greatly inhibited. Under the reaction conditions, the FTIR spectra show the presence of non-dissociatively adsorbed molecules of methanol, in addition to adsorbed methoxy, dioxymethylene, and formate species. According to the NAP XPS and XANES data, the reaction involves a reversible reduction of V⁵⁺ cations, indicating that the vanadia lattice oxygen participates in the oxidation of methanol via the classical Mars–van Krevelen mechanism. A detailed mechanism for the oxidation of methanol on vanadia catalysts is discussed.

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1. Introduction

The oxidation of methanol over V₂O₅/TiO₂ catalysts is both fundamentally and practically interesting. This reaction is a relatively simple and, nevertheless, may generate a wide range of products, such as formaldehyde, dimethyl ether, methyl formate, dimethoxymethane, and formic acid. The selectivity depends on the catalyst, reaction temperature, conversion, and partial pressures of the reactants [1–4]. For instance, unsupported and silica-supported crystallites of vanadium pentoxide demonstrate high selectivity toward formaldehvde with vields of 96–98% at the temperatures near 300–400 °C [5-8], whereas monolayer V₂O₅/TiO₂ catalysts exhibit high activity and selectivity toward methyl formate and dimethoxymethane at low temperatures (100-200 °C), with suppressed formation of formaldehyde [9-22]. All of the above-mentioned reaction products have practical significance. The production of formaldehyde via the oxidation of methanol is one of the most important industrial catalytic processes. Additionally, vanadia-based catalysts may be used to produce methyl formate and dimethoxymethane (methylal), both of which are important and versatile chemicals. Methyl formate is

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mainly used to manufacture formamide, dimethylformamide, and formic acid. Dimethoxymethane is primarily used as a solvent and for the production of perfumes, resins, adhesives, paint strippers, and protective coatings. Dimethoxymethane is an environmentally friendly material with extremely low toxicity and might also be used as a H₂ storage material for compact hydrogen generators.

Currently, the industrial production of methyl formate occurs via the carbonylation of methanol using carbon monoxide over sodium methoxide catalysts in the liquid phase. Due to the catalyst's extreme sensitivity toward water, dry CO must be used in this process. Dimethoxymethane is currently produced via a two-stage process involving (1) the oxidation of methanol to formaldehyde over silver or iron-molybdate catalysts followed by (2) condensation reactions in a methanol–formaldehyde mixture using sulfuric acid or solid acidic catalysts. The development of efficient one-step catalytic methanol oxidations in the gas phase to selectively form methyl formate or dimethoxymethane has practical applications. The V_2O_5/TiO_2 catalyst is a promising candidate for these processes.

The V₂O₅/TiO₂ system has been actively studied over the last thirty years. It has been found that vanadia can form different structures on titania surfaces depending on the vanadia content and preparation techniques [23–30]. With a vanadia content under 10% of monolayer (ML), only an isolated, monomeric structure with

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a tetrahedral coordination exists under dehydrated conditions [25,29]. Polymeric structures such as chains and ribbons of VO_x units with an octahedral coordination appear at the vanadia concentration above 20% of monolayer [29]. These structures may change under the reaction conditions via reduction/oxidation or hydration/dehydration processes; however, these changes are confined to the surface, and the migration of cations to or from the sub-surface region does not occur at ambient temperatures [25]. The incorporation of V^{4+} cations into the crystal lattice of TiO_2 has been observed at temperatures above 600 °C during the anatase-to-rutile transformation of V_2O_5/TiO_2 catalysts [31]. The monolayer coverage of polymerized vanadia species on different oxide supports was measured by Raman spectroscopy and was found to be approximately 7-8 vanadium atom/nm² for TiO₂ [27]. When the vanadium content exceeds what is necessary for the ideal monolayer, V₂O₅ crystallites are favorable. The surface vanadia species demonstrate higher catalytic activity and selectivity in many catalytic reactions compared with the V₂O₅ crystallites [32,33]. The unique properties of the surface vanadia species are related to the strong vanadia-support interaction.

This paper reports the catalytic properties of highly dispersed vanadia supported on TiO_2 (anatase) in the selective gas-phase methanol oxidation. The selectivity and reaction rates depended on the reaction temperature. Dimethoxymethane is the main reaction product below 120 °C with selectivities up to 95%. An increase in the selectivity toward methyl formate was observed above 120 °C. At 140–150 °C, methyl formate became the main reaction product with a selectivity of 80–85%. To provide further insight into the reaction mechanism, near ambient pressure X-ray photoelectron spectroscopy (NAP XPS), X-ray absorption near-edge structure (XANES), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and temperature-programmed reaction (TPR) were used. The results of these experiments led to the conclusion that the lattice oxygen is involved in the oxidation of methanol via the classical Mars-van Krevelen mechanism.

2. Experimental

2.1. Catalyst preparation

A two-step procedure was used to prepare the monolayer V_2O_5/TiO_2 catalyst. The TiO_2 support (anatase, $350 \text{ m}^2/\text{g}$) was impregnated with an aqueous solution of vanadyl oxalate via the incipient-wetness impregnation method and was subsequently dried at 110 °C for 12 h; the final calcination occurred in a flow of air for 4 h at 400 °C. This catalyst was referred to as "fresh". The fresh catalyst (20 wt% V_2O_5 and 80 wt% TiO_2) was subsequently treated in a 10% aqueous solution of nitric acid at room temperature. After the washing process, the catalyst (12.5 wt% V_2O_5 and 87.5 wt% TiO_2) was calcined in a flow of air for 4 h at 400 °C. This catalyst was referred to as "washed". The morphology of this catalyst corresponds to the structure of a so-called monolayer catalyst.

2.2. Catalytic tests

The steady-state activity of each catalyst was tested at atmospheric pressure in a differential reactor with a flow-circulating configuration [34]. The reactor was constructed from Pyrex glass tubing with a 12 mm inner diameter and a 50 mm length. A coaxial thermocouple pocket with a 4 mm outer diameter was fitted in the catalyst bed to control the temperature. The reactor was placed inside of an oven. The temperature was controlled within ±0.5 °C with a K-type thermocouple. A fraction of the catalyst powder containing grains in the size range of 0.25–0.50 mm was used. The feed consisted of methanol, oxygen, and helium in the 1:1:23 M ratio. The concentrations of reactants and products were determined with an on-line gas chromatograph (GC) equipped with thermal conductivity and flame ionization detectors. Methanol, dimethoxymethane, methyl formate, formaldehyde, formic acid, water, and CO₂ were analyzed with a Porapak T column, while the CO, oxygen, and nitrogen contents were analyzed with a NaA molecular sieve column. All gas lines from the reactor to the sampling valve were maintained at 120 °C to prevent the condensation of the reactants and products. The selectivity, *S_i*, was calculated as the molar concentration of the carbon appurtenant, *c_i*, of the product *i* divided by the sum of the concentrations of all products, *S_i* = *c_i*/ $\Sigma c_j \times 100\%$. The carbon balance was at least 97 ± 2% for all GC measurements.

2.3. Catalyst characterization

The catalysts were characterized by XRD, N₂ adsorption, elemental analysis, and FTIR spectroscopy. Powder XRD measurements were performed with a Siemens D500 diffractometer using monochromatic CuK_α radiation. The 2 θ scan covered a range of 5–70°. The specific surface area was calculated with the Brunauer–Emmett–Teller (BET) method using nitrogen adsorption isotherms measured at liquid nitrogen temperatures with an automatic Micromeritics ASAP 2400 sorptometer. The elemental analysis was performed with a Baird ICP atomic emission spectrometer. The IR spectra were recorded using a BOMEM MB-102 FTIR spectrometer. The IR samples were pellets composed of the catalysts or the TiO₂ powder pressed with CsI (2 mg of the sample and 500 mg of CsI).

2.4. In situ characterization

The chemical states of the catalysts were examined in situ using NAP XPS and XANES techniques. The experiments were performed at the synchrotron facility, BESSY II, Berlin, using the ISISS (Innovative Station for In Situ Spectroscopy) beamline. The experimental system was described in detail elsewhere [35]. The key feature of this system is the capability for in situ measurements of photoemission spectra under mbar pressures. The high brilliance of the synchrotron radiation combined with a short travel length of the photoelectrons through a high-pressure zone in the gas cell allowed us to obtain high-quality spectra at pressures up to 10 mbar under flow conditions. Powder samples were pressed into thin selfsupporting pellets and mounted on a sapphire holder between the SiC and stainless steel plates. The heating was performed from the rear with a near-infrared semiconductor laser ($\lambda = 808$ nm). The sample temperature was measured with a K-type thermocouple pressed directly against the rear of the sample. The flows of methanol and oxygen through the gas cell were regulated separately with calibrated mass-flow controllers. The total flow rate was approximately 3 sccm. During the experiments, the total pressure in the gas cell was constant 0.25 mbar. The XANES spectra were collected in the total electron yield mode. The V $2p_{3/2}$, Ti $2p_{3/2}$, C 1s, and O 1s core-level spectra were measured with a photon energy of 730 eV. The intensity of the core-level spectra was normalized to the ring current. The charge correction was performed by setting the Ti $2p_{3/}$ 2 at 459.0 eV. FitXPS software was used for curve fitting. The core-level spectra were curve fitted after a Shirley-type background subtraction assuming a Lorentzian/Gaussian line shape.

For TPR, a sample was heated at 10 K/min from 50 to 200 °C in the reaction mixture. The gas-phase products were analyzed using an on-line quadruple mass-spectrometer (Prizma QMS-200, Balzers) connected directly to the gas cell through a leak valve.

To identify the reaction intermediates involved in the oxidation of methanol, FTIR spectra were obtained in situ with the same BOMEM MB-102 spectrometer. The spectrometer was operated in the transmission mode using a specially designed quartz cell-reactor with CaF_2 windows. The cell volume was 1.5 cm³. The catalyst was pressed into a thin self-supporting pellet ($\sim 15 \text{ mg/cm}^2$) and placed into the cell-reactor. The FTIR experiments were performed at atmospheric pressure using a feed of 2 vol% CH₃OH in an air flow at 50 sccm. The spectra were recorded within 4000-1100 cm⁻¹ at a resolution of 4 cm⁻¹ at 50–180 °C. Before exposure to the reaction mixture, the sample was treated in a flow of air for 60 min at 300 °C. Subsequently, the cell-reactor and the catalyst sample were cooled to the desired temperature, and the air flow was replaced by the methanol/air mixture flow.

3. Results

3.1. Catalyst characterization

Fig. 1 presents the XRD patterns of the fresh and washed $V_2O_5/$ TiO₂ catalysts and of the TiO₂ support. All peaks observed in the TiO₂ XRD pattern can be assigned to a pure tetragonal anatase phase (JCPDS File, No. 21-1272). XRD signatures of both anatase and V₂O₅ were observed from the fresh V₂O₅/TiO₂ catalyst. The vanadia coverage was estimated from the specific surface area; the vanadia content is approximately 1.5 ML (Table 1). The washed catalyst does not exhibit the XRD reflections of the vanadia crystalline phase because the nitric acid selectively dissolved the V₂O₅ crystallites to leave only highly dispersed vanadia species on the titania surface [30]. The amount of insoluble vanadia was approximately 1 ML (Table 1). Therefore, the washed catalyst contains vanadium oxide in only a highly dispersed state.

The presence of the highly dispersed vanadia species was confirmed by FTIR for both the fresh and washed V₂O₅/TiO₂ catalysts. Fig. 2 displays the FTIR spectra of the fresh and washed catalysts, the TiO_2 (anatase) support, and bulk V_2O_5 . The anatase phase of TiO₂ exhibited broad, intense absorption bands at 260-360 and 400–850 cm⁻¹, consistent with the literature [36–38]. The spectrum of the fresh catalyst was a superposition of the anatase spectrum with weak but well-resolved bands at 800–1030 cm⁻¹. After the subtraction of the anatase spectrum, these features appeared as a sharp band at 1015 cm^{-1} and broader bands at approximately 946 and 856 cm⁻¹. Bulk V_2O_5 was characterized by the peaks at 1021, 828, 605, and 480 cm⁻¹ [36,37,39]. Therefore, the peaks at 1021 and 828 cm^{-1} were assigned to the V=O stretch and the

30 20 40 50 60 20 [deg] Fig. 1. XRD patterns obtained from TiO₂ anatase (1), fresh (2) and washed (3) V₂O₅/

TiO₂ catalysts. The marked features are from V₂O₅.

deformation of the V-O-V bridges, respectively. The broad band at approximately 600 cm⁻¹ was assigned to the bending vibrations [39.40]. The peaks at 1015 and 856 cm^{-1} in the FTIR spectrum of the fresh catalyst (Fig. 2a) confirmed the presence of the V_2O_5 crystalline phase. However, based on a comparison of the FTIR spectra of the fresh and washed catalysts, the band at 946 cm⁻¹ should be assigned to another species. Following the treatment in the nitric acid solution, the intensities of the bands at 1015 and 856 cm⁻¹ substantially decreased, whereas the band at 946 cm⁻¹ did not change (Fig. 2a). Therefore, this band might be assigned to the V-O-Ti vibration of the surface vanadate species, which is consistent with previous reports [36-38]. Note that VO_x species becomes hydrated at these conditions, and this effect leads to the significant red shift of the V=O stretching vibration. A spectrum of the washed catalyst dehydrated at 200 °C is shown in Fig. 2b. The spectrum exhibits the characteristic V=O vibration at \sim 1030 cm⁻¹.

Hence, the washed catalyst was covered with approximately 1 ML of the highly dispersed vanadia species. Typically, this catalyst is referred to as a monolayer catalyst [25]. According to the Raman spectroscopy data [41], the polymeric vanadia was the dominant species; the amount of isolated monomeric and dimeric vanadia species was negligible.

3.2. Catalytic performance

The oxidation of methanol using molecular oxygen was examined using the washed V₂O₅/TiO₂ catalysts between 70 and 150 °C. The methanol/oxygen molar ratio was maintained at 1:1. Dimethoxymethane $(H_2C(OCH_3)_2)$, methyl formate $(HCOOCH_3)$, formaldehyde (HCHO), formic acid (HCOOH), carbon oxides (CO and CO₂), and water were detected as products. No dimethyl ether or any other organic compounds were detected over the entire temperature range. The conversion and selectivity for each product at each temperature, catalyst loading, and feed flow-rate are presented in Table 2. Pure TiO₂ (anatase) did not catalyze any measurable methanol conversion up to 200 °C. This result agrees with the literature data, which indicate that TiO₂ provides a high level of methanol conversion only above 300 °C to form CO and CO₂ as the main products [42].

Table 2 also illustrates the product distribution, which depends strongly on the reaction temperature. Between 70 and 100 °C, dimethoxymethane is the major product, with a selectivity of 80-95%. Subsequently, the dimethoxymethane selectivity decreases with the reaction temperature and the reaction shifts toward methyl formate production. Between 140 and 150 °C, methyl formate becomes the main reaction product. The formation of small amounts of formaldehyde, formic acid, CO, and CO₂ was also observed. The conversion of methanol also influenced the selectivity (Table 2). Comparison of the data at 120 °C (highlighted with bold in Table 2) indicated that, at higher methanol conversions, the selectivity toward dimethoxymethane was lower and the selectivity for methyl formate was higher. For this reason, the oxidation of methanol was examined at a constant methanol conversion.

Fig. 3 demonstrates the effects of the reaction temperature on the rate and the selectivity at 50% methanol conversion. The rates of methyl formate, formaldehyde, formic acid, and CO_v formation increased with the temperature, while the dimethoxymethane yield had a maximum at 130 °C. At low temperatures, dimethoxymethane was the main reaction product. Above 120 °C, the dimethoxymethane selectivity decreased and the methyl formate selectivity increased. Methyl formate was the main reaction product between 140 and 150 °C. As shown by Busca et al. [9–11], the methyl formate selectivity decreases above 170 °C and carbon monoxide becomes the main reaction product at 190-200 °C.



Table 1

Characteristics of the fresh and washed V_2O_5/TiO_2 catalysts.

Catalyst	V ₂ O ₅ content, wt%	S_{BET} , m ² /g	V ₂ O ₅ surface density ^a , V atom/nm ²	V ₂ O ₅ surface coverage ^b , ML
Fresh	20	111	11.9	1.5
Washed	12.5	115	7.3	0.9

^a Refers to the BET area.

^b 1 ML corresponds to 7.9 V atom/nm² [27].



Fig. 2. (a) FTIR spectra of TiO₂ anatase (1), fresh (2) and washed (3) V_2O_5/TiO_2 catalysts, bulk V_2O_5 (4) after calcination at 400 °C in a flow of air, as well as difference spectra (2-1 and 3-1), which were obtained via direct subtraction of spectrum 1 from spectra 2 and 3, respectively. The samples were pellets composed of the catalysts or the TiO₂ powder pressed with Csl. (b) FTIR spectra of thin self-supported pellets of the washed catalyst obtained at 25 °C (1) and 200 °C (2) in air.

Table 2			
Catalytic properties of the washed	V ₂ O ₅ /TiO ₂ catalyst	during the oxidation	of methanol ^a

Temp, °C	Catalyst loading, g	Feed flow, l/h	Conversion, %	Selectivity, %					
				DMM ^b	MF ^c	$\mathbf{F}^{\mathbf{d}}$	FA ^e	СО	CO ₂
70	2.0	2.5	10.0	95	5.0	0	0	0	0
100	2.0	2.5	17.0	90	10.0	0	0	0	0
120	2.0	2.5	30.1	75	19.4	2.5	3.1	0	0
130	2.0	2.5	44.0	43	46.7	4.0	2.3	3.0	1.0
140	2.0	2.5	60.0	3	83.9	3.6	2.5	5.5	1.5
100	2.0	4.5	10.0	94	6.0	0	0	0	0
120	2.0	4.5	20.5	80	17.0	3	0	0	0
140	2.0	4.5	45.0	8.2	78.5	5.0	3.1	4.1	1.1
100	7.5	2.5	45.0	80	20.0	0	0	0	0
120	7.5	2.5	59.7	57	32.8	2.0	5.1	3.1	0
130	7.5	2.5	73.5	15	74.5	2.5	4.0	4.0	0.0
140	7.5	2.5	85.0	1	82.5	3.0	3.0	8.5	2.0

^a The molar methanol/oxygen ratio was 1:1.

^b DDM is dimethoxymethane.

^c MF is methyl formate.

^d F is formaldehyde.

^e FA is formic acid.

3.3. In situ FTIR study

Fig. 4 presents the FTIR spectra acquired under the steady-state conditions during the oxidation of methanol at different temperatures. A reaction mixture of 2 vol% CH₃OH in air was passed through the IR cell-reactor loaded with the washed V₂O₅/TiO₂ catalyst. The spectrum from the catalyst before exposure to the reaction mixture and the spectrum from gas-phase methanol were subtracted from the raw IR spectra to identify the contributions

of the adsorbed surface species. At temperatures up to 120 °C, the methoxy species ($-OCH_3$) is the most abundant reaction intermediate. This conclusion was drawn from the observation of two intense bands at 2931 and 2825 cm⁻¹, which corresponded to the symmetric stretching v_s(CH₃) mode and the Fermi resonance of 2 δ_s (CH₃) of the adsorbed methoxy species, respectively [9,13,43–49]. The bands at 2955 and 2847 cm⁻¹ could be assigned to the same vibration modes of non-dissociatively adsorbed methanol [9]. The shoulder at 2970 cm⁻¹ can be attributed to the



Fig. 3. Effect of reaction temperature on the selectivity (right side) and the rate $(10^{-9} \text{ mol m}^{-2} \text{ s}^{-1})$ of formation (left side) of dimethoxymethane (DMM), methyl formate (MF), formaldehyde (F), formic acid (FA), and CO_x. Conversion of methanol was 50%.



Fig. 4. FTIR difference spectra of the washed V₂O₅/TiO₂ catalyst obtained during the oxidation of methanol at different temperatures: 1 – 50 °C, 2 – 100 °C, 3 – 120 °C, 4 – 140 °C, 5 – 160 °C, 6 – 180 °C.

asymmetric stretching mode $v_{as}(CH_3)$ of the methyl group in the methoxy species. The symmetric and asymmetric deformation vibrational modes $\delta(CH_3)$ at 1433 and 1447 cm⁻¹, as well as the rocking vibration mode $\rho(CH_3)$ at 1150 cm⁻¹ detected in the low frequency region, also corresponded to the methoxy species [9]. In addition, bands assigned to the surface dioxymethylene (CH_2O_2) species [46] were detected at 2923 and 2884 cm⁻¹. The spectrum obtained at 50 °C displays an intense band at 1627 cm⁻¹ attributed to the bending mode of the adsorbed water molecules. Simultaneously, a strong band was observed at 3400 cm⁻¹ (not shown) corresponding to the stretching vibration v(OH) of adsorbed water and adsorbed molecular methanol. When the temperature increased from 50 to 120 °C, no significant changes were observed in the intensities of the vibrational bands attributed to the surface methoxy and dioxymethylene species. Above 140 °C, the peaks at 1550, 1360, and 1655 cm^{-1} began to dominate in the spectrum. The two former peaks were characteristic of the $v_{as}(0-C-0)$ and $v_s(0-C-0)$ modes of a bidentate formate species, and the feature at 1655 cm^{-1} was due to the stretching vibration v(C=O) of adsorbed methyl formate [9,13,49]. The vibrational frequencies are summarized in Table 3.

The methanol adsorption on the TiO₂ support was also investigated between 100 and 170 °C. Fig. 5 displays the typical FTIR spectrum of the adsorbed species on the pure TiO₂ (anatase) after the methanol adsorption at 100 °C. The intense peaks at 2960, 2925, 2831, and 1462 cm⁻¹ correspond to the CH₃ stretching and bending modes of the adsorbed molecular methanol and methoxy species [9,13]. No peaks characteristic of the adsorbed formaldehyde, dioxymethylene, and formate species were detected between 100 and 170 °C. These results agree with the low activity of TiO₂ during the oxidation of methanol.

3.4. In situ NAP XPS, XANES, and TPR study

In situ NAP XPS and XANES techniques could be used under mbar pressures [35,50–52]. The comparison of the spectroscopic data with the kinetics measurements performed in the flow reactor at atmospheric pressure (Table 2 and Fig. 3) is only possible if there is no pressure gap. The TPR technique was applied to verify this statement. The washed V_2O_5/TiO_2 catalyst was heated inside the in situ XPS reaction gas cell in the equimolar CH₃OH/O₂ mixture and in pure methanol at a total pressure of 0.25 mbar; the product

Table 3	
IR bands and assignments of the surface species formed during the ox	idation of methanol on the V_2O_5/TiO_2 catalyst

Frequency, cm ⁻¹	Type of surface species	Type of vibration	Ref.
1150	Methoxy species	Rocking $\rho(CH_3)$ mode	[9]
1360	Bidentate formate species	Symmetric stretching $v_s(O-C-O)$ mode	[9,13,49]
1433	Methoxy species	Symmetric deformation $\delta(CH_3)$ mode	[9]
1447	Methoxy species	Asymmetric deformation $\delta(CH_3)$ mode	[9]
1550	Bidentate formate species	Asymmetric stretching $v_{as}(O-C-O)$ mode	[9,13,49]
1655	Methyl formate	Stretching $v(C=0)$ mode	[9,13,49]
2825	Methoxy species	Fermi resonance of $2\delta_s(CH_3)$	[9,13,43-49]
2847	Molecular methanol	Fermi resonance of $2\delta_s(CH_3)$	[9]
2884	Dioxymethylene species	Symmetric stretching $v_s(CH_2)$ mode	[46]
2923	Dioxymethylene species	Asymmetric stretching $v_{as}(CH_2)$ mode	[46]
2931	Methoxy species	Symmetric stretching $v_s(CH_3)$ mode	[9,13,43-49]
2955	Molecular methanol	Symmetric stretching $v_s(CH_3)$ mode	[9]
2970	Methoxy species	Asymmetric stretching $v_{as}(CH_3)$ mode	[9]



Fig. 5. FTIR difference spectra of TiO₂ (anatase) obtained during the adsorption of methanol at 100 °C.

distribution was monitored with a differentially pumped massspectrometer (Fig. 6). The catalyst was pretreated in 0.25 mbar of flowing O_2 at 300 °C for 30 min.

The detection of formaldehyde and CO with a mass-spectrometer was hindered due to overlap in the methanol fragmentation pattern. However, the presence of formic acid, methyl formate, and dimethoxymethane among the products was unambiguously proven by the mass-spectrometric signals with m/z of 45, 60, and 75, respectively. Within the reaction mixture (Fig. 6a), the yield of dimethoxymethane displayed a maximum at 95 °C and subsequently decreased. The methyl formate yield reached its maximum at approximately 130 °C. The formic acid exhibited steady growth above 130 $^\circ\text{C}.$ The maximum for dimethoxymethane was also detected at 95 °C in the experiment using pure methanol (Fig. 6b); however, in the absence of O_2 , the methyl formate formation was suppressed and formic acid formation was facilitated above 130 °C. Therefore, the catalytic behavior under mbar pressure follows the same trends as observed under atmospheric pressure (Table 2, Fig. 3); the results of the in situ NAP XPS and XANES study are therefore fully applicable.

The NAP XPS and XANES spectra were measured during heating the V_2O_5/TiO_2 catalyst in the step-wise manner in both the equimolar CH₃OH/O₂ mixture and pure methanol. The main NAP XPS results for the washed catalyst are summarized in Table 4. The $V 2p_{3/2}$ and $V L_{2,3}$ -edges XAS spectra, along with the Ti $2p_{3/2}$ core-level and Ti $L_{2,3}$ -edges XAS spectra, are presented in Figs. 7 and 8, respectively. Before exposure to the reaction mixture, the catalyst was pretreated in 0.25 mbar of flowing O₂ for 30 min at 300 °C inside the in situ XPS reaction gas cell. This treatment generated the fully oxidized vanadium species: only a narrow single peak at 517.7 eV corresponding to the V⁵⁺ state was observed under the oxygen atmosphere (Fig. 7a). A new V $2p_{3/2}$ peak at 516.4-516.5 eV appears in the reaction mixture, pointing to the partial reduction of V⁵⁺ to V⁴⁺, even at room temperature. It should be noted that in highly cited studies [53-57], the vanadium ions in the vanadium oxides, such as V_2O_5 , V_2O_4 , and V_2O_3 , are characterized by the $V 2p_{3/2}$ binding energies in the ranges of 516.9–517.2, 515.7-516.2, and 515.2-515.7 eV, respectively. However, the latest studies have reported higher binding energy values of $V 2p_{3/2}$ at 517.3–517.7 and 516.2–516.5 eV for bulk and supported V_2O_5 , as well as for V₂O₄, respectively [20,58–64]. These numbers agree with our data.

Fig. 7b displays the V $L_{2,3}$ -edges XAS spectra obtained during the same experiment. The transition energy and the line shape are sensitive to the chemical environment and can be used as a fingerprint for the vanadium oxidation state [65,66]. Because the selection rules for the electron transition during photon absorption require $\Delta l = \pm 1$, the peaks at 518–519 and 524–525 eV in the XANES



Fig. 6. TPR spectra measured in an equimolar CH₃OH/O₂ mixture (a) and in methanol (b) with a total pressure of 0.25 mbar.

 Table 4

 Binding energies and FWHMs of the Ti 2p_{3/2} and V 2p_{3/2} peaks shown in Figs. 7a, 8a, and 9; the relative intensity of the different components (%) are shown in parentheses.

Mixture	<i>T</i> , °C	FWHM of Ti $2p_{3/2}$, eV	V 2p _{3/2} , eV (%)			
			V ⁵⁺	V ⁴⁺	V ³⁺	
02	300	1.12	517.66 (100)	-1	-	
$CH_3OH + O_2$	100	1.05	517.73 (51)	516.50 (49)	-	
$CH_3OH + O_2$	150	1.07	517.68 (59)	516.43 (41)	-	
$CH_3OH + O_2$	200	1.09	517.63 (67)	516.40 (33)	-	
CH ₃ OH	50	1.10	-	516.60 (41)	515.54 (59)	
CH ₃ OH	100	1.12	-	516.60 (31)	515.42 (69)	
CH ₃ OH	150	1.13	-	516.60 (28)	515.45 (72)	
CH₃OH	200	1.14	-	516.50 (32)	515.47 (68)	



Fig. 7. Normalized V $2p_{3/2}$ core-level spectra (a) and V $L_{2,3}$ -edges XAS spectra (b) of the washed V₂O₅/TiO₂ catalyst measured in 0.25 mbar O₂ at 300 °C (1), as well as in the equimolar CH₃OH/O₂ mixture with a total pressure of 0.25 mbar at 100, 150, and 200 °C (2, 3, and 4); 2-1 is the difference XAS spectrum obtained via the direct subtraction of spectrum 1 multiplied on the factor 0.5 from spectrum 2, respectively.



Fig. 8. Normalized Ti $2p_{3/2}$ core-level spectra (a) and Ti $L_{2,3}$ -edge XAS spectra (b) of the washed V₂O₅/TiO₂ catalyst measured in 0.25 mbar O₂ at 300 °C (1), as well as in the equimolar CH₃OH/O₂ mixture with a total pressure of 0.25 mbar at 100, 150, and 200 °C (2, 3, and 4), respectively.

spectra presented in Fig. 7b can be roughly assigned to the electronic excitations from the spin–orbit split levels $2p_{3/2}$ (L_3 -edge) and $2p_{1/2}$ (L_2 -edge) into the empty or partially occupied vanadium 3*d* orbitals. The L_3 -edge spectrum of the fully oxidized vanadia obtained in pure oxygen exhibits a well-defined fine structure with at least four distinct resonances. The observed line shape is typical of bulk V₂O₅ [66,67]. The position of the main resonance at 518.9 eV is very similar to the value reported for bulk V₂O₅ [66].

Under the reaction conditions, the V $L_{2,3}$ -edge shifts toward lower energies and the line shape changes. To identify the fine structure, the difference XAS spectra were analyzed. Because only half of the V⁵⁺ cations were reduced to V⁴⁺ under the reaction conditions according to the NAP XPS measurements (Table 4), a corresponding difference spectrum was obtained by subtracting the spectrum of the fully oxidized vanadia multiplied by 0.5 from the spectrum of the partially reduced vanadia (Fig. 7b). The difference L₃-edge spectrum was shifted toward lower energies and has a different line shape. Only two distinct resonances were observed in the spectrum: the main resonance at 517.8 eV and a well-distinguished shoulder at 515.9 eV. A similar line shape has been reported for bulk VO₂ [66,68,69]. Additionally, according to the correlation between the oxidation state and the L_3 -edge peak position of the binary vanadium oxides, this resonance corresponds to the V^{4+} state [70,71]. Chen et al. [70] reported that the V L_3 -edge position shifted by 0.7 eV for every ionic charge within the range from 515.5 eV (metallic vanadium) to 519.0 eV (V₂O₅). In the current study, the shift was approximately 0.8 eV, corresponding to the partial reduction of V^{5+} to V^{4+} . Therefore, the XANES data proved that the partial reduction of V^{5+} to V^{4+} occurred under these reaction conditions.

No changes were detected in the Ti 2p core-level and Ti *L*-edges XAS spectra under the reaction conditions from room temperature to 200 °C. These data indicate that titanium in the support remains in the Ti⁴⁺ state. The narrow Ti $2p_{3/2}$ peaks with the full width at half maximum (FWHM) of approximately 1.1 eV were at 459.0 eV (Table 4), which is typical for bulk TiO₂ (Fig. 8a). According to the literature data [72–77], pure TiO₂ is characterized by the Ti $2p_{3/2}$ binding energy in the range of 458.7–459.2 eV, while the binding energy for the Ti³⁺ species is between 456.2 and 457.4 eV. The X-ray absorption spectra are displayed in Fig. 8b. The spectra were normalized to the same maximum peak height.

The spectra reveal a well-defined fine structure with at least seven distinct resonances. The main near-edge structure of the spectra was assigned to the $2p^63d^0 \rightarrow 2p^5c3d^1$ dipole transition, where c represents the 2p core hole [78]. Similar to vanadium, the 2p spin-orbit coupling splits the initial state into $2p_{3/2}$ and $2p_{1/2}$, resulting in two *L*-edge features denoted as L_3 and L_2 , respectively. Both the L_3 and L_2 features were further split into the t_{2g} and e_{2g} components because of the low symmetry of the ligand field. The L_3-e_{2g} feature also splits into a doublet (peak D and E in Fig. 8b) because of slight distortions in the TiO₆ octahedra among the titania polymorphs resulting from the configurational deformation predicted by the Jahn-Teller theorem [79]. Detailed descriptions of the Ti *L*-edges spectra can be found in the literature [80,81]. The different polymorphs of TiO₂ could be distinguished via the relative intensities of the D/E doublet [79,82,83]. For example, in the anatase structure, the intensity of the D peak was substantially stronger than the intensity of the E peak, whereas it would have been the opposite in the rutile structure. In this study, all of spectra shown in Fig. 8b are identical; their shape corresponds to the previously reported Ti L-edges spectra of anatase [79,82,83], meaning that, during the oxidation of methanol, the Ti⁴⁺ cations were octahedrally coordinated in the TiO₂ anatase phase.

The results presented above clearly indicate that, during the oxidation of methanol, the partial reduction of V^{5+} to V^{4+} occurs but the titanium cations remain in the Ti⁴⁺ state. The curve fitting of the V $2p_{3/2}$ spectra (Fig. 7a) indicated that the relative contribution of different vanadium oxidation states depended on the temperature; the quantitative data are presented in Table 4. Increasing the temperature from 100 to 200 °C caused more than a 15% decrease in the V^{4+} fraction. The catalyst underwent complete reduction from V^{5+} to V^{4+} and V^{3+} after exposure to methanol at 0.25 mbar, even at room temperature. This conclusion arose from the analysis of the V $2p_{3/2}$ spectra of the washed V₂O₅/TiO₂ catalysts presented in Fig. 9. In the methanol atmosphere, the typical V $2p_{3/2}$ spectrum of the fully oxidized V⁵⁺ catalyst exhibiting a single peak transformed into a spectrum with two peaks: one at 516.5-516.6 and the other at 515.4-515.5 eV, which can be attributed to V^{4+} and V^{3+} , respectively. The fraction of the V^{3+} state grows slightly when the temperature increases (Table 4). The following treatment in oxygen at 300 °C led again to the full oxidation of the vanadium to V⁵⁺. These data indicate that supported vanadium



Fig. 9. Normalized V $2p_{3/2}$ core-level spectra of the washed V₂O₅/TiO₂ catalyst measured in 0.25 mbar O₂ at 300 °C (1), as well as in 0.25 mbar CH₃OH at 50, 100, 150, and 200 °C (2, 3, 4, and 5), respectively.

could undergo reversible oxidation and reduction during the oxidation of methanol.

Fig. 10 displays the C1s core-level spectra that were measured in situ concurrent with the V $2p_{3/2}$ and Ti $2p_{3/2}$ spectra. The oxygen treatment fully removed carbon-contained species from the catalyst surface. In the reaction mixture and in pure methanol, the catalyst surface was covered with different carbon-contained species. In the reaction mixture (Fig. 10a), three components of the C 1s spectrum could be distinguished at 285.3–285.4, 286.1–286.2, and 286.9–287.2 eV. The most intense component at *ca*. 286 eV corresponded to the methoxy species [4]. The weaker component at *ca*. 285 eV was assigned to C–C–O coupling products and/or to hydrocarbon impurities, which can accumulate on the surface during XPS measurements. The third component at *ca.* 287 eV was assigned to dioxymethylene. In agreement with the FTIR data, the amount of the methoxy species decreased with increasing temperature. A similar trend was observed for the V⁴⁺ state (Table 4), indicating that the formation of the methoxy species on the vanadia surface was accompanied by the partial reduction of V⁵⁺ to V⁴⁺.

The C 1s spectra obtained in pure methanol (Fig. 10b) revealed additionally a weak peak at 288.9 eV, which was assigned to the surface formate species, and a sharp peak at 287.6–287.8 eV, which could be assigned mainly to gas-phase methanol [4] (the pressure was high enough to observe the gas-phase signals). The FWHM of the peak at 287.6–287.8 eV was about 0.65–0.85 eV, whereas the FWHM of the other peaks is in the range of 1.5–1.8 eV. According to our previous studies, such sharp peaks are usually observed for molecules in the gas phase [35,51]. In this case, a significant fraction of vanadium was in the V³⁺ state (Table 4). We conclude that the formation of the formate species on the vanadia surface causes the partial reduction of V⁴⁺ to V³⁺; however, the presence of oxygen led to a fast re-oxidation of V³⁺ to V⁵⁺ (Fig. 10a).

4. Discussion

The catalytic and spectroscopic data obtained in this study clarified the detailed mechanism for the oxidation of methanol over vanadia–titania catalysts proposed by Busca et al. [9–13]. A review of this mechanism has been previously published [84]. The combined data from the in situ surface sensitive techniques, such as NAP XPS and XANES, with FTIR, TPR, and kinetics measurements allowed us to include the variations of vanadium's chemical state in the reaction mechanism. The proposed scheme is illustrated in Fig. 11. The active sites are assigned to the highly dispersed vanadia species VO_x on TiO₂. The polymeric vanadium oxide species prevail in the monolayer V₂O₅/TiO₂ catalyst. These species consist of a terminal V=O bond with at least one V–O–Ti and one or two bridging V–O–V bonds.

Under the mild conditions, dimethoxymethane and methyl formate are the main products formed over the V_2O_5/TiO_2 catalyst. The vibration bands at 2955 and 2847 cm⁻¹ at low reaction temperatures (Fig. 4) indicate that the first step of the catalytic cycle



Fig. 10. C 1s core-level spectra of the washed V_2O_5/TiO_2 catalyst measured in 0.25 mbar O_2 at 300 °C (1), as well as in an equimolar CH₃OH/ O_2 mixture (a) and pure CH₃OH (b) at 100, 150, and 200 °C (2, 3, and 4), respectively; a total pressure was 0.25 mbar; all the spectra were normalized to the V 2p integral intensity.



Fig. 11. Proposed mechanism for the oxidation of methanol over highly dispersed vanadia supported on TiO₂.

is the adsorption of methanol. Methanol chemically adsorbs by donating the electron density from the oxygen atom to a surface V⁵⁺ cation. Methanol adsorption via the hydrogen bonding with the surface hydroxyl groups or the lattice oxygen atoms could not be ruled out as well. Subsequently, the adsorbed methanol dissociates to form the surface methoxy and hydroxyl groups (stage 1 in Fig. 11), which was confirmed by FTIR (Fig. 4). The partial reduction of the vanadium cations from the V⁵⁺ to V⁴⁺ state was detected by NAP XPS and XANES (Fig. 7). The methoxy species may be described as a monodentate structure with a covalent-like bond to the vanadium cation [9.44]. The main question in this model is the position of oxygen atom, which takes a proton and transforms to the hydroxyl group. Kilos et al. [85] studied the oxidation of ethanol over VO_x/Al₂O₃ and suggested that ethanol dissociates over vanadia to form adsorbed ethoxide species and OH groups that bond with adjacent vanadium atoms. In contrast, Beck et al. [86] studied the oxidation of ethanol over supported VO_x and suggested that the hydroxyl group bonds with cations of the support. According to theoretical studies of the oxidation of methanol over VO_{y} supported on titania, the hydroxyl group bonds with a titanium atom [87,88]. We suppose that in our monolayer catalyst, which consisted of polymeric VO_x species, the methoxy group probably coordinated to a vanadium cation, whereas H atom could be transferred to oxygen of the V-O-Ti bond to form the Ti-OH group (stage 1 in Fig. 11).

Due to the further loss of the hydrogen atom, the methoxy species transforms into molecularly adsorbed formaldehyde, and this event is accompanied by the partial reduction of the second vanadium cation to V^{4+} (stage 2 in Fig. 11). In light of the recent investigations [86,87,89], we believe that the formation of formaldehyde occurs via the transfer of an H atom of a methoxy group to the O atom of the V=O group. The hydroxyl groups recombine to generate water (stage 3 in Fig. 11).

Depending on the temperature, formaldehyde can desorb as a product or undergo further transformations to form dioxymethylene species (stage 4 in Fig. 11). The dioxymethylene species were detected on the V_2O_5/TiO_2 catalyst by FTIR spectroscopy (Fig. 4). Because only a minor amount of gas-phase formaldehyde was detected by gas chromatography at 130 °C (Table 2) and a large amount of the surface dioxymethylene species was observed during the formaldehyde oxidation on the same catalyst at 70 °C [46,90], the formation of the dioxymethylene species from the adsorbed formaldehyde species is likely a rapid process.

The reaction of the dioxymethylene species with the methoxy species or methanol generates dimethoxymethane, which is the main reaction product at low temperatures (Table 2). This reaction most likely proceeds through the nucleophilic attack to the dioxymethylene carbon atom by the oxygen atoms from an adjacent methoxy species or from an adsorbed methanol molecule [91]. This proposal is consistent with the high selectivity observed toward dimethoxymethane at temperatures up to 120 °C. At this temperature, the surface was covered with the dioxymethylene species, molecularly adsorbed methanol, and the methoxy species (Fig. 4).

At higher temperatures, the dioxymethylene is oxidized to generate the formate species (stage 5 in Fig. 11). The formation of the formate species is accompanied by the reduction of vanadium cations to the V³⁺ state observed by XPS under the methanol atmosphere (Fig. 8). In the methanol/oxygen mixture, the V^{3+} cation was not detected because the re-oxidation of V^{3+} to form V^{4+} and/or V⁵⁺ is rapid in the presence of gas-phase oxygen. The formate species may transform into formic acid and carbon monoxide [9] or may react with methanol to generate methyl formate. As shown by FTIR, the concentration of the dioxymethylene species decreases above 120 °C, while the intensities of the stretching vibrations for the formate species (1550 and 1360 cm^{-1}) and the intensity of the adsorbed methyl formate band at 1655 cm⁻¹ increase (Fig. 4). In good agreement with this mechanism, the V₂O₅/TiO₂ catalysts demonstrate high selectivity during the oxidation of formaldehyde to generated formic acid under similar conditions [30,46,90]. The formate species is stable in helium up to 180 °C, but readily decomposes in oxygen at 100–150 °C, producing formic acid [46]. A similar behavior was observed during the in situ XPS study. The formate species were identified in the C 1s spectra measured in methanol (Fig. 10b), whereas the presence of oxygen in the reaction mixture leads a decreased concentration of the adsorbed formate species below the XPS detection limit (Fig. 10a). As a result, the formation of formic acid was observed in the TPR experiments (Fig. 6).

Re-oxidation of the vanadium active sites by dioxygen completes the catalytic cycle (stage 6 in Fig. 11). Although it is difficult to explain how O_2 molecules transforms into lattice O^{2-} species on monolayer V_2O_5/TiO_2 catalysts, the re-oxidation of V^{3+} and V^{4+} to V^{5+} during the oxidation of methanol in the presence of O_2 was clearly observed by XPS (Figs. 7 and 8, Table 4). Most probably, the rapid re-oxidation of reduced vanadia can occur via the adsorption of O_2 at a vacancy site to form a peroxide species; one of two oxygen atoms eliminates the vacancy, while the other oxygen atom migrates across the support surface until it reaches and eliminates a secondary vacancy [92]. The re-oxidation of the catalyst surface should restore its adsorption properties because methanol adsorbs mainly on the V⁵⁺ sites. Therefore, the fully oxidized vanadia should be more active than the partially reduced species. This hypothesis is confirmed because the methanol conversion on the V-Ti oxide catalyst at 175 °C gradually decreases from 100% to approximately 30% when the molar methanol/oxygen ratio increases from 0.5 to 2.7 [9,11]. This also agrees with the data reported by Wang and Madix [93], who have shown using TPRS that the fully oxidized surface in a model monolayer $V_2O_5/TiO_2(110)$ catalyst has a much higher activity in the oxidation of methanol to formaldehyde compared with the reduced surface with vanadium oxidation states of V^{3+} and V^{4+} .

The presented data follow the proposal that the selective oxidation of methanol on the monolayer V_2O_5/TiO_2 catalyst occurs at the redox V^{n+} sites via the Mars–van Krevelen mechanism [94], which involves the lattice oxygen species (see the proposed scheme in Fig. 11). Final proof of this mechanism requires the comparison of the methanol oxidation rate over the V₂O₅/TiO₂ catalyst in the presence and in the absence of oxygen [95], which is the subject of a future work.

5. Conclusions

The highly dispersed vanadia species on TiO₂ are active and selective catalysts for the oxidation of methanol to methyl formate and dimethoxymethane under mild conditions. At low temperatures (70–100 °C), dimethoxymethane is the main reaction product with the 88–95% selectivity, while at higher temperatures (150 °C), methyl formate becomes the main reaction product with the 85% selectivity. The production of formaldehyde is greatly inhibited at temperatures below 150 °C.

Combining the catalytic measurements with in situ FTIR, NAP XPS, XANES, and TPR provided additional insight into the mechanism for the oxidation of methanol. The FTIR data revealed the presence of molecularly adsorbed methanol, in addition to the adsorbed methoxy, dioxymethylene, and formate species. NAP XPS and XANES demonstrated that the reaction involves the reversible reduction of V⁵⁺ cations, proving that the lattice oxygen participates in the oxidation of methanol via the classical Mars-van Krevelen mechanism, which consists of the reduction of the catalyst surface by methanol and its subsequent re-oxidation by oxygen from the gas phase. The reaction begins with the molecular chemisorption of methanol on the V⁵⁺ cations. The adsorbed molecules dissociate to form the methoxy species and hydroxyl groups, which is accompanied by the reduction of the vanadium cations from the V⁵⁺ to V⁴⁺ state. The oxidation (H abstraction and electron transfer) of the methoxy species leads to the formation of adsorbed formaldehyde, which can desorb as the product or transform into the surface dioxymethylene species. The reaction of the dioxymethylene species with either the methoxy species or methanol generates dimethoxymethane, which is the main product at low temperatures. At higher temperatures, dioxymethylene transforms into the formate species, which may also react with methanol to furnish methyl formate. The formation of the formate species is accompanied by the reduction of the vanadium to V³⁺. The catalytic cycle is completed by re-oxidizing the vanadium cations to the V⁵⁺ state with molecular oxygen from the gas phase.

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