

Chemistry, spectroscopy and the role of supported vanadium oxides in heterogeneous catalysis

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Abstract

Supported vanadium oxide catalysts are active in a wide range of applications. In this review, an overview is given of the current knowledge available about vanadium oxide-based catalysts. The review starts with the importance of vanadium in heterogeneous catalysis, a discussion of the molecular structure of vanadium in water and in the solid state and an overview of the spectroscopic techniques enabling to study the chemistry of supported vanadium oxides. In the second part, it will be shown that advanced spectroscopic tools can be used to obtain detailed information about the coordination environment and oxidation state of vanadium oxides during each stage of the life-span of a heterogeneous catalyst. Three topics will be discussed: (1) the molecular structure of supported vanadium oxide catalysts under hydrated, dehydrated and reduced conditions, including the parameters, which influence the molecular structures formed at the surface of the support oxide; (2) elucidation of the active surface vanadium oxide during the oxidation of methanol to formaldehyde, the reaction mechanism and the vanadium oxide–support effect; and (3) deactivation of fluid catalytic cracking (FCC) catalysts by migration of vanadium oxides and the development of a method preventing the structural breakdown of zeolites by trapping the mobile vanadium oxides in an aluminum oxide coating.

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1. Introduction

Vanadium was discovered in 1801 in Mexico by the Spanish mineralogist A.M. del Rio, who considered it to be present in a particular brownish lead mineral [1–3]. He named the new element erythronium. However, the French chemist H.V. Collet-Descotils incorrectly declared that this new element was only impure chromium. Later on, in 1830, the Swedish chemist N.G. Sefström rediscovered the element and named it in honor of Vanadis, the old Norse name for the

Scandinavian goddess Freyja—a fertility goddess—because of its beautiful multicolored compounds. In 1831, vanadium was unambiguously identified as the originally named erythronium element of del Rio and the lead mineral is now known as vanadinite ($\text{Pb}_5(\text{VO}_4)_3\text{Cl}$).

Vanadium is one of the most abundant and widely distributed metals in the earth's crust and is found in about 152 different minerals, in certain iron ores and also in the form of organic complexes in some crude oils, e.g. V–porphyrin complexes [4,5]. The major sources of vanadium are titaniferrous magnetite ores from mines in Australia, China, Russia and South Africa. The current level of the annual production of vanadium in the world is 38,000 tonnes. About 80%

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of the vanadium produced is used as steel additive, as it makes steel shock- and vibration-resistant. Vanadium is also an essential element in aerospace industry, as it guarantees low density, high strength and resistance to high operating temperatures and stress. Titanium–aluminum–vanadium alloys are used in, e.g. aero-engine gas turbines and in the undercarriages of planes. Other uses of vanadium are in ceramics and electronics. Vanadium salts are well known for the brilliant orange and blue colors in ceramics or in dyes for textiles and leather.

The most dominant non-metallurgical use of vanadium is in catalysis, which represents about 5% of the annual production of vanadium. Table 1 summarizes some industrial catalytic processes based on vanadium oxides. Vanadium oxide-based catalysts are used in the manufacture of important chemicals (e.g. sulfuric acid, phthalic anhydride) and in the reduction of environmental pollution (e.g. nitrogen oxides from flue gas of power plants) and is the most important metal used in metal oxide catalysis [6–13]. The importance of vanadium in supported metal oxide catalysis is further underlined by Fig. 1. This figure summarizes the number of papers (expressed as a percentage of the total number of papers) of several transition metals in the field of metal oxide catalysis, which can be found in the open literature [14].

Most catalysts based on vanadium oxide consist of a vanadium oxide phase deposited on the surface of an oxide support, such as SiO_2 , Al_2O_3 , TiO_2 and ZrO_2 . Supporting a metal oxide on the surface of another oxide was initially proposed to improve the catalytic activity of the active metal oxide phase due to a gain in surface area and mechanical strength [7,15]. The support was considered as inert substance that provided a high surface to carry the active metal oxide

Table 1

Industrial catalytic processes using vanadium oxides [6–13]

Industrial process	Catalyst material
Oxidation of SO_2 to SO_3 in the production of sulfuric acid	V_2O_5
Oxidation of benzene to maleic anhydride	V_2O_5
Oxidation of naphthalene to phthalic anhydride	V, Mo oxides
Oxidation of butene to phthalic anhydride	V, P oxides
Oxidation of <i>o</i> -xylene to phthalic anhydride	V, Ti oxides
Selective reduction of NO_x with NH_3	$\text{V}_2\text{O}_5/\text{WO}_3/\text{TiO}_2$

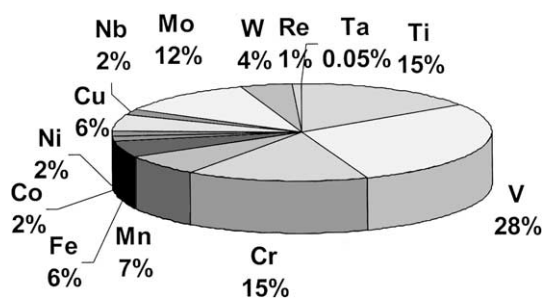


Fig. 1. Overview of the importance of vanadium in supported metal oxide catalysis. The numbers are based on an extensive open literature search in the period 1967–2000.

component or to improve the mechanical strength of the catalyst material. However, during the last decade catalyst scientists have unambiguously shown that the activity and selectivity of supported metal oxide catalysts are significantly affected by the properties of the support oxide material. This is generally known as the metal oxide–support effect, although its exact origin and mechanism of operation is still unclear.

The fundamental basis for the catalytic performances of supported vanadium oxides lies in the variability in geometric and electronic structure of surface vanadium oxides. Fundamental knowledge about the chemistry of supported vanadium oxides is of key importance in heterogeneous catalysis and spectroscopic tools are necessary to build up this knowledge. In this review paper, the fundamental advances into the surface chemistry and spectroscopy of vanadium oxides in heterogeneous catalysts of the last decade are emphasized. No exhaustive discussion of all the catalytic applications of supported vanadium oxides available in the open literature will be given (Table 2) [16–59]. Rather, we want to develop fundamental concepts, which explain the differences in chemistry of supported vanadium oxides during each stage of the life-span of a heterogeneous catalyst, i.e. synthesis, calcination, activation, catalytic operation and deactivation. The review paper starts with a short introduction on the molecular structures of vanadium oxides in water and in the solid state. In the second part, several spectroscopic methods for the characterization of supported vanadium oxides are discussed, together with their potential and limitations. The third part deals with an overview of the methods for preparing supported vanadium oxide catalysts. The

Table 2

Overview of the reactions catalyzed by supported vanadium oxides as described in the open literature

Catalytic reaction	References
Selective oxidation of alkanes and alkenes	[16,17]
Selective catalytic reduction of NO _x with NH ₃	[18–20]
Oxidation of <i>o</i> -xylene to phthalic anhydride	[21,22]
Ammonoxidation of aromatics and methylaromatics	[23–25]
Selective oxidation of methanol to formaldehyde	[26]
Oxidation of SO ₂	[27–29]
Decomposition of isopropylalcohol	[30]
Oxidation of aliphatic and aromatic hydrocarbons	[31,32]
Photo-oxidation of CO	[33]
Photo-isomerization of butene	[34]
Partial oxidation of methane to formaldehyde	[35–37]
Oxidation of H ₂ S	[38,39]
Synthesis of isobutyraldehyde from methanol and ethanol	[40]
Selective oxidation of 4-methylanisole	[41]
Selective oxidation of <i>p</i> -methoxytoluene	[42]
Alkylation of aldehydes with methanol	[43]
Oxidative coupling of methane	[44]
Synthesis of 2,6-dimethylphenol from methanol and cyclohexanone	[45]
Synthesis of isobutyraldehyde from methanol and <i>n</i> -propylalcohol	[46,47]
Total oxidation of benzene	[48]
Dehydrocyclodimerization of isobutene to xylene	[49]
Polymerization of olefins	[50]
Selective oxidation of alkanes with peroxides	[51]
Oxidative dehydrogenation of alkanes	[52–54]
Isomerization of <i>m</i> -xylene	[55]
Epoxidation of alkenes with peroxides	[56]
Hydroxylation of phenol	[57]
Direct conversion of methane to aromatics	[58,59]

paper continues with a discussion of three examples, in which spectroscopic tools are of paramount importance to unravel the surface chemistry and reactivity of vanadium oxides in heterogeneous catalysis. The paper ends with some concluding remarks and a look into the future.

2. Molecular structures of vanadium oxides in water and in the solid state

Supported vanadium oxides show chemical and electronic properties, which are entirely different from those found for unsupported vanadium pentoxide (V₂O₅), in aqueous media and in the solid state [1–3]. In order to fully appreciate these differences,

a brief overview of the molecular structure of vanadium oxides in water and in the solid state has to be given. Vanadium has the electron configuration [Ar] 3d³ 4s². The main oxidation states are +2, +3, +4 and +5. V⁵⁺ (d⁰) can be present in tetrahedral (VO₄), pentahedral (VO₅) and octahedral (VO₆) coordination environment and tends to form polyoxoanions. V⁴⁺ (d¹) is also stable and is mostly present in square pyramidal or pseudo-octahedral coordination as an isolated cation. Other oxidation states such as V³⁺ (d²) and V²⁺ (d³) are less stable and only present under reducing conditions.

2.1. Molecular structures of vanadium oxides in aqueous media

The most important oxidation states in aqueous solution are V⁵⁺ and V⁴⁺. The specific vanadium oxide species that can exist depend on the solution pH and the vanadium oxide concentration. This is illustrated for V⁵⁺ in Fig. 2, which shows the different regions in which a particular vanadium oxide species is stable [60]. This scheme is generally known as the Pourbaix diagram. V⁵⁺ hydrolyses in a very complex way and 12 different species—monomeric as well as polymeric species—are known to exist in aqueous solutions. V⁴⁺ is particularly stable as the vanadyl ion (VO²⁺), which is one of the most stable oxy-metal ions. In water it appears in the form of a tetragonal bipyramidal coordination (VO(H₂O)₅²⁺). Other V⁴⁺ species hydrolyze to give dimeric species, even in dilute solutions (10⁻³ M). V²⁺ as well as V³⁺ are unstable and are oxidized by water and air, respectively. Little is known about the V²⁺ species, while V³⁺ ions are present as hexa-aquo species in acidic solutions.

2.2. Molecular structures of vanadium oxides in the solid state

The principal vanadium oxides are V₂O₅, VO₂, V₂O₃ and VO. In these oxides, the formal oxidation state of vanadium decreases from +5 to +2. Other more exotic vanadium oxide compounds are mixed valence oxides, such as V₃O₅, V₄O₇ and V₇O₁₃, and have the general formula V_nO_{2n-1}.

V₂O₅ is an orange-red and acidic oxide, in which the vanadium ions are present in distorted octahedrons. The structure of V₂O₅ is often approximated

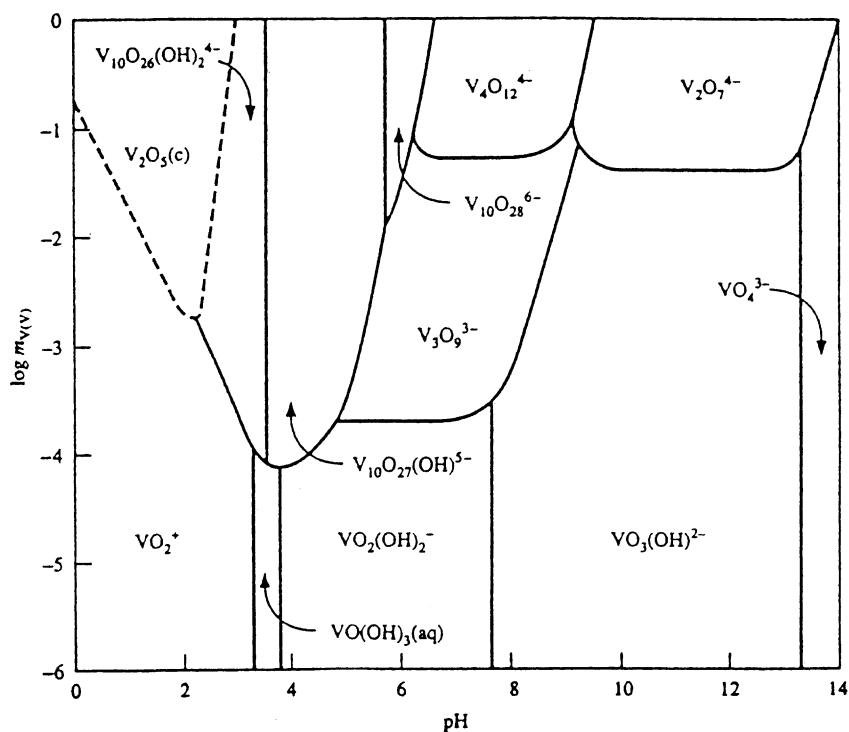


Fig. 2. The Pourbaix diagram of vanadium, expressing the vanadium speciation as a function of pH and potential at 25 °C and an ionic strength of 1 M.

by zigzag ribbons of square pyramids of VO_5 . Each vanadium atom and its five nearest oxygen neighbors create VO_5 -pyramids, which share their corners, building double chains along the b -direction. These chains are connected by their edges and the resulting layers are stacked along the c -direction. As a result, a vanadium oxide unit consists of an octahedrally coordinated VO_6 , with three distinct vanadium–oxygen bond distances (Figs. 3 and 4d) [6]. The vanadium ion is slightly displaced from the basal plane towards the apex of the pyramid, which creates a strong and short $\text{V}=\text{O}_{(1)}$ bond of 1.58 Å. The $\text{V}-\text{O}_{(3)}$ distance in opposite direction is much longer (2.79 Å). The four $\text{V}-\text{O}_{(2)}$ bonds to the oxygen in the basal plane have a length of 1.83 Å. V_2O_5 is only slightly soluble in water, resulting in a pale yellow solution with some colloidal character. It also dissolves in NaOH to give colorless solutions containing the vanadate ion, VO_4^{3-} . On acidification, a complicated series of reactions occur involving the formation of hydroxanions and polyanions (e.g. decavanadate), as

shown in Fig. 2. In very strong acid solutions, the dioxovanadium or pervanadyl ion (VO_2^+) is formed.

The dark blue VO_2 oxide is obtained by mild reduction of V_2O_5 and has a rutile-like structure distorted by the presence of pairs of vanadium atoms bonded together. One bond, the $\text{V}=\text{O}$ bond, is much shorter than the others in the VO_6 unit. It is an amphoteric oxide, dissolving in non-oxidizing acids to give the

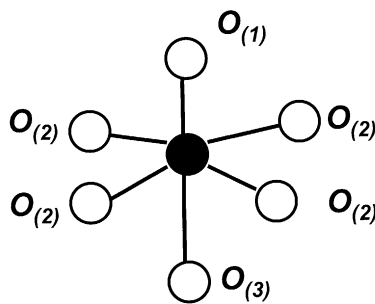


Fig. 3. Molecular structure of V^{5+} in V_2O_5 crystals indicating three different V–O distances.

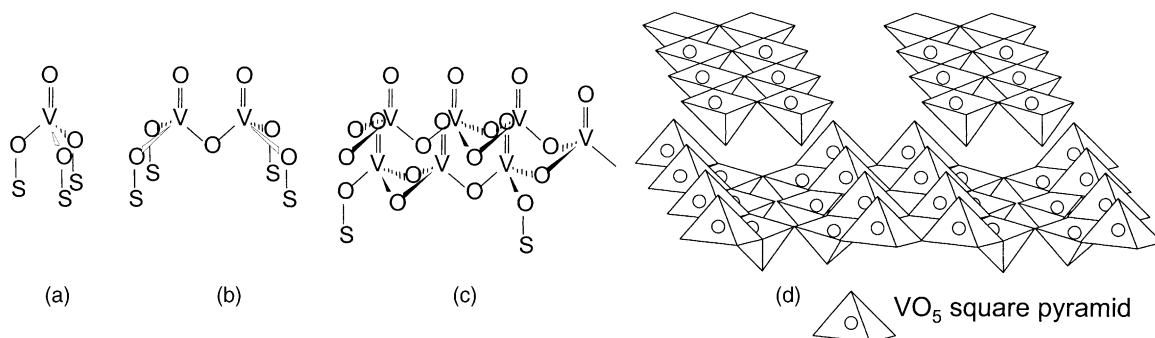


Fig. 4. Possible molecular configurations for supported vanadium oxides (with S the support cation): (a) isolated vanadium oxide species; (b) dimeric vanadium oxide species; (c) two-dimensional vanadium oxide chains; (d) V_2O_5 crystals.

blue VO^{2+} , which appears in water in the form of a tetragonal bipyramid of the form $VO(H_2O)_5^{2+}$. In alkali media, it will transform to the yellow to brown $V_4O_9^{2-}$ or at high pH to VO_4^{4-} . The black V_2O_3 has a corundum structure and is basic. It is obtained by reduction of V_2O_5 with hydrogen or carbon monoxide, but is often oxygen deficient without change in structure. It dissolves in aqueous acids to give blue or green V^{3+} solutions, which are strongly reducing. From these solutions addition of hydroxyl ions gives the hydrous oxide, which is very easily oxidized in air. The grey-colored VO or V_2O_2 has somewhat metallic behavior and possess a defect rock-salt structure. It is prone to non-stoichiometry and can dissolve in mineral acids to give violet air-sensitive V^{2+} solutions. The oxidation of V^{2+} by air is complicated and appears to proceed in part by direct oxidation to VO^{2+} and in part by way of an intermediate species of type VOV^{4+} .

3. Characterization methods for supported vanadium oxides

The characterization of the molecular structures of supported vanadium oxides is rather involved, since deposition of this metal oxide on an inorganic oxide can result in

- (1) isolated vanadium ions;
- (2) dimeric or polymeric species;
- (3) chains of vanadium ions building up a two-dimensional over-layer of supported vanadium oxides;

- (4) three-dimensional vanadium oxides (e.g. V_2O_5), crystalline or not; and
- (5) mixed metal oxide phases with the support (e.g. ZrV_2O_7), or a combination of the above-mentioned molecular structures.

Different vanadium oxide configurations are shown in Fig. 4. Useful characterization techniques, which can provide detailed information about the molecular structure of supported vanadium oxides, must be capable of discriminating between these different vanadium oxide configurations and of quantifying the individual oxidation states [61–64]. The spectroscopic techniques used in the literature for studying supported vanadium oxides are summarized in Table 3, together with the information about detectable oxidation states, dispersion, coordination and quantitative determination [65]. It is clear from Table 3 that no characterization technique will be capable of providing all the information needed for a complete characterization. Thus, successful characterization of vanadium oxides in heterogeneous catalysts requires a multi-technique approach. In what follows, a brief overview of the capabilities and limitations of these characterization techniques is given.

The infrared spectroscopy (IR) technique provides information on the molecular structure of the supported vanadium oxide catalysts, although the investigation of the surface vanadium oxide vibrations is often complicated due to the overlapping infrared bands of the support oxide [66–75]. IR can also probe the interaction of vanadium oxide with the surface hydroxyl groups of the oxide support since hydroxyl groups give rise to intense infrared

Table 3
Spectroscopic techniques for studying supported vanadium oxides and the obtained information on coordination states, and dispersion [61–65]

Spectroscopic technique	Potentials				Limitations/comments
	Oxidation state	Coordination	Dispersion	Quantitative	
Infrared spectroscopy (IR)	+	+	–	+/-	Vanadium oxide vibrations are often overshadowed by the support vibrations; small molecules (e.g. CO) indirectly probe the coordination environment of the metal ion
Raman spectroscopy (RS)	+	+	+/-	–	The Raman effect is not a sensitive process and as a consequence low vanadium oxide loadings are difficult to study; fluorescence may be a problem especially with reduced samples
Electron spin resonance (ESR)	+	+	+/-	+	Only applicable to paramagnetic nuclei (e.g. V ⁴⁺)
X-ray photoelectron spectroscopy (XPS)	+	–	+	+	Only surface sensitive; need for UHV conditions
Nuclear magnetic resonance (NMR)	–	+	–	+	Quenching problems may occur in the presence of paramagnetic metal ions
Diffuse reflectance spectroscopy (DRS) in the UV-Vis-NIR region	+	+	–	+	Broad and overlapping absorption bands complicate spectrum interpretation; quantitative measurements only possible at low vanadium oxide loadings
X-ray absorption fine structure spectroscopy (XAFS)	+	+	+/-	–	Average coordination numbers are obtained; complicated data analysis

absorption bands. The technique is also frequently used to study the interaction of the catalyst material with reactant molecules during adsorption or surface studies. Examples are the oxidation reactions of methanol and toluene. The adsorption of basic molecules, such as ammonia and pyridine, is a useful method to determine the surface acidity of the catalyst as it enables to distinguish between Brønsted and Lewis acid sites. Oxidation states of supported vanadium oxides, namely V^{3+} and V^{4+} , can be determined by adsorption of NO at low temperature (e.g. -180°C).

The Raman spectroscopy (RS) technique can discriminate between different vanadium oxide coordination environments and bond lengths [76–86]. Vanadium–oxygen vibrations are present below 1100 cm^{-1} and RS has the advantage that the support oxides only show weak absorption bands in the $700\text{--}1100\text{ cm}^{-1}$ region. Indeed, silica and alumina supports show any or only very weak Raman bands in the range $1100\text{--}100\text{ cm}^{-1}$, whereas titania and zirconia oxides possess strong Raman absorption bands in the region below 700 cm^{-1} . Interaction of the vanadium oxides with the support hydroxyls cannot be easily studied with RS since the hydroxyl groups of the support oxides are weak Raman scatterers. Only for titania and silica sometimes weak hydroxyl groups can be observed. Various studies have demonstrated that the simultaneous use of reference vanadium oxide compounds and the correlation between Raman frequency and bond length makes RS very well suited to study the molecular structures of supported vanadium oxides. RS can also be applied to study structural changes during in situ conditions, although it is not very sensitive to reduced vanadium oxides (e.g. V^{4+} and V^{3+}) due to their low Raman cross-sections. The surface vanadium oxide structure has been studied during the adsorption and oxidation of methanol and methane, and during the selective catalytic reduction of nitrogen oxides. The influence of water vapor on the surface vanadium oxide structure has also been investigated.

Electron spin resonance (ESR) is a powerful and quantitative technique to study especially the presence and coordination geometry of the paramagnetic V^{4+} (d^1) species even under in situ conditions [87–96]. Vanadium has a nuclear spin of $\frac{7}{2}$, resulting in a complex spectrum with a high number of hyperfine lines. This hyperfine splitting, arising from the interaction

of the unpaired electron with the vanadium nucleus is sensitive to the chemical environment around the paramagnetic V^{4+} ion. Therefore, ESR is very well suited to characterize the molecular structure of surface V^{4+} species, whereas V^{3+} (d^2) ions can only be studied at very low temperatures since the energy difference between the ground and excited state is too small. The fact that only V^{4+} species can be observed in an easy way can be regarded both as an advantage and a disadvantage. Spin–spin coupling at high vanadium oxide loading may lead to inaccurate quantitative determinations of V^{4+} species.

X-ray photoelectron spectroscopy (XPS) provides information about the oxidation state and the chemical environment of a given atom due to shifts in the binding energies [97–105]. The structural information is, however, limited since XPS cannot discriminate between different VO_x structures possessing the same oxidation state, i.e. between VO_6 , VO_5 and VO_4 . Other disadvantages are the use of ultrahigh vacuum conditions, which may result in the reduction of surface vanadium species in the measurement chamber and the fact that the technique only provides information about the catalyst surface. In contrast, the vanadium oxide to support oxide ratio provides information on the dispersion of the vanadium oxide phase and the dimension of the vanadium oxide crystals at the catalyst surface. In addition, the technique allows verifying impurities (e.g. K, Na and Cl) potentially present in the catalyst material.

Solid state ^{51}V nuclear magnetic resonance (NMR) is a suitable technique to investigate supported V^{5+} oxides since the nuclear spin of vanadium is $\frac{7}{2}$, its natural abundance is almost 100% and its capability to discriminate between different coordination environments of vanadium oxides [106–115]. The presence of paramagnetic species, such as V^{4+} , may prevent to observe NMR signals since such species broadens the NMR signal, and consequently, the signal due to V^{5+} can be lost. ^{51}V NMR has been used to characterize supported vanadium oxides on, e.g. silica, alumina, titania and zirconia. The limitation of the technique is the somewhat lower sensitivity, especially when compared with ESR techniques.

The diffuse reflectance spectroscopy (DRS) technique in the UV-Vis-NIR region provides insight on the different oxidation states and coordination geometries of supported vanadium oxides [116–120]. The

DRS technique probes the charge transfer transitions as well as the d–d transitions of vanadium ions at the catalyst surface. The technique is quantitative at least for low vanadium oxide loadings and can be used under in situ conditions. The disadvantage is that the DRS signals are usually broad and overlap with each other, leading to a biased spectral analysis. In addition, the origin of the specific electronic transition is sometimes difficult to isolate due to its dependence on the local coordination environment, the polymerization degree and the specific oxidation state.

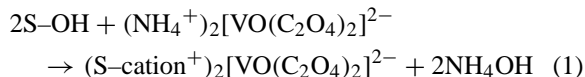
The X-ray absorption fine structure spectroscopy (XAFS) technique, including EXAFS and XANES, provides detailed information on the oxidation state and the coordination environment of supported vanadium oxides [121–129]. Bond distances and coordination numbers can be determined with high precision and no long range ordering is required as in the case of X-ray diffraction. The XAFS technique can be used under in situ conditions. Disadvantages are that advanced data analysis is required to extract the information from the spectra and that only an average structure can be inferred, which is often a problem since supported vanadium oxides can co-exist in different coordination environments and oxidation states.

4. Preparation methods of supported vanadium oxide catalysts

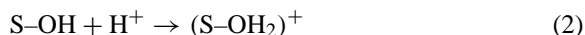
Supported vanadium oxide catalysts can be prepared via several methods [6]. In the following paragraphs, the most important preparation techniques will be briefly described, and their advantages and disadvantages will be discussed.

Impregnation is the most simple and widely used preparation technique for making supported vanadium oxide catalysts. The term impregnation denotes a procedure whereby a certain volume of an aqueous or non-aqueous solution containing a vanadium compound is adsorbed into the pores of an inorganic oxide. Two impregnation procedures can be distinguished. If the support is dipped into an excess amount of solution, the process is called wet impregnation. More precise control over the vanadium oxide loading is achieved with a technique called dry impregnation, pore volume impregnation or incipient wetness impregnation. The support is then contacted with a

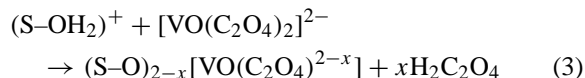
solution of appropriate concentration, corresponding in quantity to the total known pore volume of the support, or slightly less. This allows precise control of the concentration of the active vanadium oxide component on the support. However, the maximum loading obtainable in a single impregnation is limited by the solubility of the reagent and if necessary multiple impregnation steps should be applied. V₂O₅ has a low solubility in aqueous and non-aqueous solutions and therefore, many authors prepare their supported vanadium oxide catalysts by impregnating the support with either an aqueous solution of, e.g. NH₄VO₃ [130–137] or NH₄VO₃ dissolved in aqueous oxalic acid [138–141]. The impregnation process is followed by a drying and heating step in which the vanadium oxide compound is chemically anchored onto the support oxide. This is illustrated in Fig. 5a. In the latter case, the resulting deep blue solution contains the compound (NH₄)₂[VO(C₂O₄)₂], the vanadium being in the +4 oxidation state [142]. The advantage of this method is that much higher amounts of NH₄VO₃ can be dissolved since this compound is poorly soluble in water. The oxalic acid acts as a reducing agent, which results in the formation of V⁴⁺. The interaction of this ionic oxalate complex with the support (denoted as S) can proceed via an ion exchange reaction [143]:



As the sorption of these complexes is carried out from acid solutions with a pH < 2, the surface hydroxyl groups are protonated and the support surface possesses a positive charge:



A ligand substitution reaction can now take place together with the ion exchange mechanism. Ligand substitution implies the exchange of ligands of the metal complex for functional groups of the support oxide:



Non-aqueous impregnation methods use, e.g. vanadyl acetylacetonate (VO(acac)₂) as vanadium compound or VO(OC₂H₅)₃ or VO(OC₃H₇)₃ in methanol or another organic solvent [144–148]. The latter method is

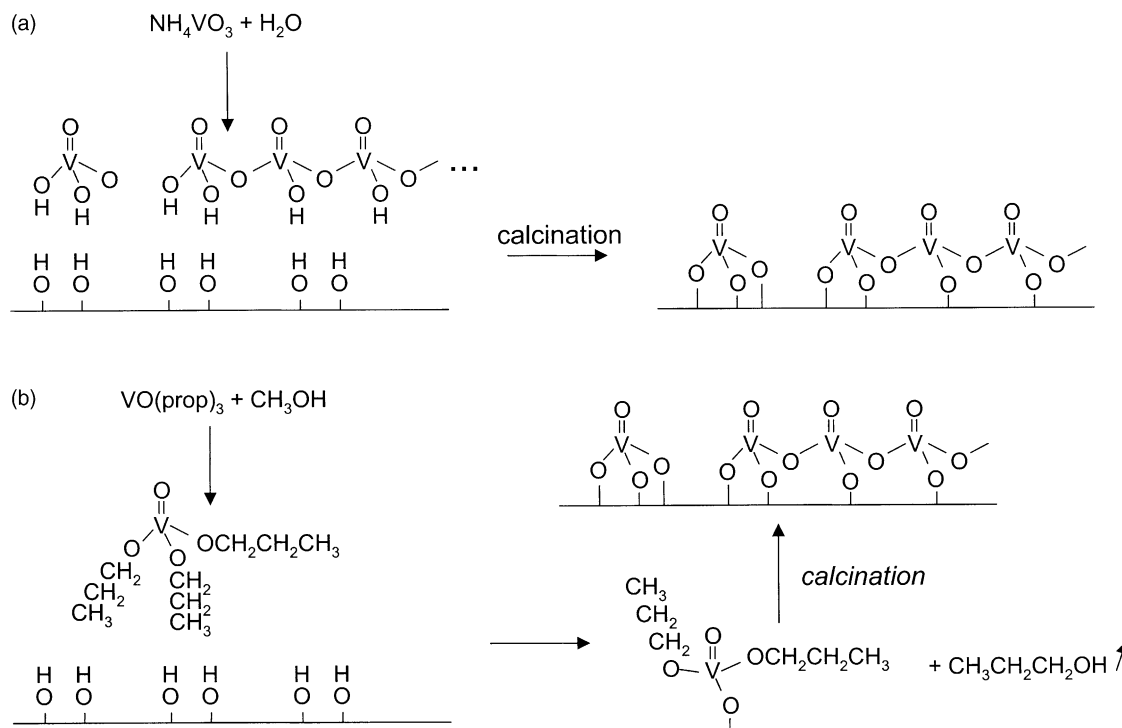


Fig. 5. Synthesis methods for the preparation of supported vanadium oxide catalysts: (a) impregnation with an aqueous solution of NH_4VO_3 , followed by calcination in oxygen and (b) impregnation with $\text{VO}(\text{OC}_3\text{H}_7)_3$ in methanol, followed by calcination in oxygen or air and release of propanol.

illustrated in Fig. 5b. After the impregnation step the material is calcined in air at high temperatures (e.g. 500°C) and surface anchored vanadium oxides are formed.

Grafting is defined as the removal from solution of a compound containing vanadium through interaction with hydroxyl groups on the surface of an inorganic support. Many authors have used a solution of VOCl_3 in CCl_4 or in benzene to obtain a dispersed VO_x phase on various inorganic oxides [149]. Non-aqueous solutions of $\text{VO}(\text{O}^i\text{Bu})_3$ have also been successfully used [150–153]. Multiple grafting followed by calcination will result in a monolayer of vanadium oxides on the surface of a support oxide. A related technique is chemical vapor deposition (CVD), which makes use of a volatile inorganic or organo-metallic compound that is deposited at the surface of a support oxide by reaction with the support hydroxyl groups. Interesting vanadium precursor compounds for this preparation method are VCl_4 and VOCl_3 , and their interaction

with SiO_2 , TiO_2 and Al_2O_3 has been studied in detail [154–157]. A similar synthesis method is atomic layer deposition (ALD) and series of V/SiO_2 and $\text{V}/\text{Al}_2\text{O}_3$ catalysts were prepared according to this gas phase preparation technique [158].

Vanadium oxides and support oxides—or their precursors—may be co-precipitated from a solution containing compounds of each element. This usually produces an intimate mixing of the catalytic active phase and the support, but the active component is dispersed through the bulk as well as being on the surface. An example of such procedure is the preparation of V/TiO_2 catalyst materials starting from a mixed V^{4+} and Ti^{4+} solution and by adding NH_4OH . A final preparation technique is the method of thermal spreading [159,160]. This technique makes use of the high mobility of V_2O_5 with a Tamman temperature of 370°C . Heating of, e.g. a physical mixture of V_2O_5 and Al_2O_3 , will lead to the spreading of vanadium oxides over the alumina support and the formation

of different surface vanadium oxide configurations. The driving force for this spreading phenomenon is the lowering of the surface free energy by forming a monolayer of surface vanadium oxide species on the high surface free energy oxide support. Formation of such monolayer is also observed during hydrocarbon oxidation reactions over physical mixtures of V_2O_5 and TiO_2 [161,162].

Although many different synthesis methods have been used in preparing supported vanadium oxide

catalysts, all supported vanadium oxide catalysts were found to contain essentially the same vanadium oxide configurations after prolonged calcination treatments [163]. This means that the preparation method does not influence the local coordination environment of supported vanadium oxides. However, it influences the amount of supported vanadium oxides, which can be deposited on a particular support oxide without the formation of crystalline V_2O_5 . Thus, the preparation method may affect the vanadium oxide dispersion.

Table 4

Influence of the synthesis method on the maximum vanadium oxide loading, which can be dispersed on a particular support oxide without formation of V_2O_5 crystals

Support oxide	Preparation method	Surface area of support (m^2/g)	Maximum loading of vanadium (V atoms per nm^2 of support)	Detection method	Reference
SiO_2	Impregnation with NH_4VO_3	150	0.7	NMR	[164]
	Impregnation with NH_4VO_3	200	1.0	RS	[165]
	Impregnation with NH_4VO_3	200	1.0	NMR	[166]
	Impregnation with NH_4VO_3	300	0.6	RS	[167]
	Impregnation with NH_4VO_3	530	0.2	RS	[168]
	Impregnation with NH_4VO_3	350	0.4	XRD	[169]
	Impregnation with ammonium vanadyl oxalate	530	0.4	RS	[77]
	Impregnation with ammonium vanadyl oxalate	90	1.0	RS	[170]
	Impregnation with ammonium vanadyl oxalate	203	1.0	XRD	[156]
	Impregnation with ammonium vanadyl oxalate	90	1.0	RS	[171]
Al_2O_3	Grafting with VCl_3	160	0.5	EXAFS	[172]
	Chemical vapor deposition with $VO(OC_2H_5)_3$	203	3.9	XRD	[156]
	Impregnation with NH_4VO_3	205	8.0	NMR	[164]
	Impregnation with NH_4VO_3	262	2.2	XRD	[173]
	Impregnation with NH_4VO_3	78	5.6	RS	[167]
	Impregnation with NH_4VO_3	187	5.0	XRD	[174]
	Impregnation with NH_4VO_3	145	6.5	NMR	[175]
	Impregnation with NH_4VO_3	101	3.1	XRD	[176]
	Impregnation with NH_4VO_3	100	4.4	RS	[170]
	Impregnation with NH_4VO_3	188	2.3	XRD	[177]
TiO_2	Grafting with VCl_3	80	9.4	EXAFS	[172]
	Chemical vapor deposition with $VO(OC_2H_5)_3$	93	18.0	XRD	[156]
	Grafting with $VO(OC_2H_5)_3$	180	1.8	NMR	[106]
	Impregnation with NH_4VO_3	45	8.3	RS	[167]
	Impregnation with NH_4VO_3	35	7.1	XRD	[174]
	Impregnation with NH_4VO_3	50	13.0	XRD	[169]
	Impregnation with ammonium vanadyl oxalate	50	7.8	RS	[178]
	Impregnation with ammonium vanadyl oxalate	52	1.7	RS	[77]
	Impregnation with ammonium vanadyl oxalate	50	5.6	RS	[170]
	Impregnation with ammonium vanadyl oxalate	59	7.2	XRD	[177]
ZrO_2	Impregnation with ammonium vanadyl oxalate	98	6.6	RS	[179]
	Impregnation with ammonium vanadyl oxalate	120	8.0	EXAFS	[172]
	Grafting with VCl_3	120	8.0	EXAFS	[172]
	Impregnation with NH_4VO_3	71	3.5	XRD	[174]
	Impregnation with NH_4VO_3	49	3.5	XRD	[100]
ZrO_2	Impregnation with ammonium vanadyl oxalate	63	0.8	RS	[180]
	Impregnation with ammonium vanadyl oxalate	330	7.5	RS	[181]
	Impregnation with ammonium vanadyl oxalate	140	7.0	RS	[182]

Table 4 illustrates this observation by comparing the maximum amount of vanadium (V per nm²), which can be deposited on SiO₂, Al₂O₃, TiO₂ and ZrO₂ without V₂O₅ crystal formation [6]. The results were obtained from publications of different research groups active in supported vanadium oxide catalyst chemistry [164–182]. It is clear that different characterization techniques can be used to detect V₂O₅ crystal formation, namely XRD, NMR, RS and XAFS, but each of these techniques has its own sensitivity towards V₂O₅ crystals. RS and NMR are much more sensitive in this respect than XRD and XAFS. The maximum amount of vanadium without V₂O₅ formation is also a function of the support type, the preparation method and the research group who was preparing the catalyst material (Table 4). The maximum amount of deposited surface vanadium oxides without V₂O₅ crystal formation is around 0.5–1 V per nm² for V/SiO₂ catalysts and around 5–10 V per nm² for V/ZrO₂, V/TiO₂ and V/Al₂O₃ catalysts. These values should be compared with the monolayer surface coverage value of 4.98 molecules of V₂O₅ per nm² based on the crystal structure of V₂O₅. From the V–O bond length of crystalline V₂O₅ one can then estimate that a two-dimensional polyvanadate oxide layer and isolated monomeric vanadium oxide layer corresponds to a surface density of 10 and 2.5 V per nm², respectively.

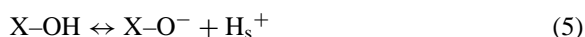
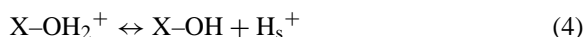
5. Chemistry of surface vanadium oxides during the different stages of the life-span of a heterogeneous catalyst

The goal of this section is to illustrate that spectroscopic techniques are very powerful to elucidate the surface chemistry of supported vanadium oxides during each stage of the life-span of a heterogeneous

catalyst starting from its genesis up to the deactivation of the catalyst material [65,183]. This will be done by presenting several examples on catalyst synthesis, calcination, activation, operation and deactivation, mainly from our own or collaborative work.

5.1. Catalyst synthesis

The molecular structures of vanadium oxide species on amorphous support oxides after impregnation have been studied in detail with Raman spectroscopy by Deo and Wachs [184]. These authors have shown that the surface vanadium oxide molecular structures were found to depend on the net pH at which the oxide surface possesses no surface charge (point of zero charge, pzc). The net surface pH at pzc or the isoelectric point (IEP) of a specific support is mainly determined by its composition (SiO₂, Al₂O₃, ZrO₂, TiO₂ and MgO). Under hydrated conditions, the surface of an amorphous oxide is covered by a thin water film and its hydroxyl population is subject to pH-dependent equilibria reactions:



where X = Si, Al, Zr, Ti or Mg; H_s⁺ and H⁺ represent the surface and solution proton, respectively. The IEP of different amorphous support oxides are summarized in Table 5. The lower the IEP of the amorphous oxide, the more the equilibria of the reactions (4)–(6) are driven to the right. The higher the H⁺ concentration near the surface, the more the equilibrium reactions in aqueous solutions are driven towards the formation of more polymerized vanadium oxide species. Hence, the structure of the vanadium oxide

Table 5
Surface vanadium oxide species, as detected by Raman spectroscopy, on different hydrated amorphous inorganic oxides [183]

Support oxide	IEP	Surface area (m ² /g)	V oxide at low V loading	V oxide at high V loading
MgO	11.0	80	VO ₄ ^a , V ₂ O ₇ , (VO ₃) _n	VO ₄ ^a , V ₂ O ₇ ^a , (VO ₃) _n
Al ₂ O ₃	8.9	180	(VO ₃) _n ^a	(VO ₃) _n , V ₁₀ O ₂₈ ^a
TiO ₂	6.2	55	(VO ₃) _n ^a , V ₁₀ O ₂₈ ^a	V ₁₀ O ₂₈ ^a
ZrO ₂	5.9	39	V ₂ O ₇ , (VO ₃) _n ^a , V ₁₀ O ₂₈ ^a	V ₁₀ O ₂₈ ^a
SiO ₂	3.9	300	O _h ^b	V ₂ O ₅

^a Major species.

^b Decavanadate-like environment, from solid-state ⁵¹V NMR spectroscopy.

species follows the vanadium(V) oxide aqueous chemistry as a function of the pH (i.e. the Pourbaix diagram as shown in Fig. 2), and the main spectroscopic results for low-loaded supported vanadium oxide catalysts are summarized in Table 5, which confirm the above-mentioned reasoning.

When the vanadium oxide loading increases two effects come into play: (1) the pH near the surface is lowered due to the presence of acidic vanadium oxides, and decreases with increasing vanadium oxide loading; and (2) the dispersion depends on the available surface area as well as the availability of surface hydroxyl groups. Both factors influence the chemistry of vanadium in the same direction, i.e. toward the formation of surface polyvanadates. In other words, the following sequence is observed for increasing vanadium oxide loading: orthovanadate (VO_4) \rightarrow pyrovanadate (V_2O_7) \rightarrow metavanadate (VO_3) $_n$ \rightarrow decavanadate ($\text{V}_{10}\text{O}_{28}$) \rightarrow vanadium pentoxide (V_2O_5). Effect (2) also implicates that high surface area supports, such as alumina, will give rise to relatively less polymerized vanadium oxide species ($\text{V}_{10}\text{O}_{28}$) at high vanadium oxide loadings because more surface area is available to accommodate monovanadate species. The effect of the presence of additives, such as P_2O_5 and K_2O , can alter the IEP of the supports or form vanadium phosphate or potassium vanadate compounds, and consequently, change the vanadium oxide speciation [185].

Recent EXAFS studies have revealed that the above-described surface chemistry is more complex than stated and that vanadium oxides are present in a kind of supported liquid phase covering the surface of the amorphous oxides [186]. More specifically, there is direct spectroscopic evidence for the interaction of vanadium oxides in the supported liquid phase and the support oxygen atoms. EXAFS indicates that the vanadium oxide–support oxygen distance is a function of the support oxide, i.e. 2.60 Å for Nb_2O_5 and 3.01–3.05 Å for Al_2O_3 supports. More efforts should be directed towards the development of a more detailed model describing such supported liquid phase of hydrated vanadium oxides.

5.2. Catalyst calcination

Upon heating in air, the water molecules adsorbed on the support and around the supported vanadium

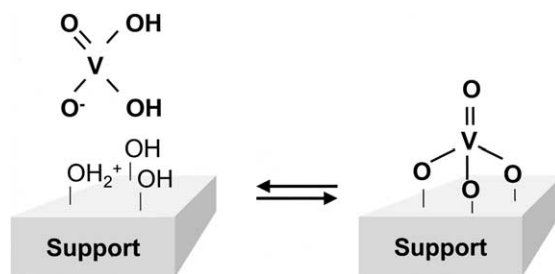


Fig. 6. Anchoring of hydrated vanadium oxides onto a support oxide via an esterification reaction with the hydroxyl groups.

oxides are removed and the supported vanadium oxides are oxidized mainly to the +5 oxidation state. The formed dehydrated vanadium oxides directly anchor onto the surface via an esterification reaction with the hydroxyl groups of the amorphous oxide, resulting in the formation of surface vanadium oxides. This is schematically drawn in Fig. 6. Direct evidence for this reaction comes from IR spectroscopy indicating the consumption of hydroxyl groups, which is proportional with the quantity of deposited vanadium oxides. Turek et al. [187] have shown that on alumina this reaction starts from the more basic OH groups to the more acidic groups.

As already mentioned above, the supported vanadium oxide species formed on various supports all essentially possess the same molecular structures [9,183,188]. At low surface vanadium oxide loading the supported vanadium oxides are isolated VO_4 units, containing one terminal mono-oxo $\text{V}=\text{O}$ bond and three bridging vanadium–oxygen–support bond with symmetry C_{3v} . The mono-oxo nature of this species has been concluded from O-18 isotopic labeling experiments in conjunction with Raman spectroscopy [189]. In addition, the frequency of the $\text{V}=\text{O}$ bond has the same value in IR and Raman spectroscopy. XAFS spectroscopy has shown that the $\text{V}=\text{O}$ bond is around 1.62 Å, whereas the three $\text{V}-\text{O}$ –support bonds have each a length of about 1.81 Å [186]. The $\text{V}=\text{O}$ bond distance can also be deduced from the corresponding Raman stretching frequencies by applying empirical correlations based on the diatomic approximations as developed by Hardcastle and Wachs [86]. The support oxide has some effect on the mono-oxo $\text{V}=\text{O}$ bond length, which varies in the range 1.60–1.79 Å depending on the support oxide material.

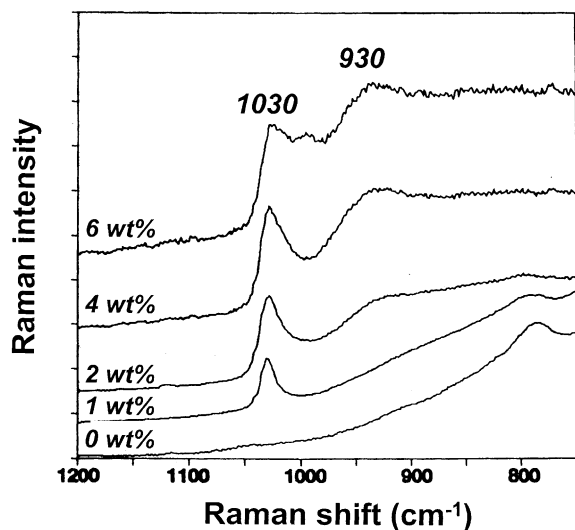


Fig. 7. Raman spectra of calcined V/Al₂O₃ catalysts as a function of vanadium oxide loading.

With increasing surface vanadium oxide loading, the amount of dimeric and polymeric chains of VO₄ units will gradually increase. The polymeric vanadium oxide species consist of a terminal V=O bond with one V–O–support and two bridging V–O–V bonds (Fig. 4c). Fig. 7 illustrates this trend by showing the Raman spectra of dehydrated V/Al₂O₃ catalysts with an increasing amount of vanadium oxide. It can be seen that the Raman band at 930 cm⁻¹, due to the presence of polymeric vanadium oxides, gradually increases with increasing vanadium oxide loading. At very high vanadium oxide loadings, a fraction of the supported vanadium oxide species are present in an octahedral coordination (VO₆ units), which can aggregate to form amorphous and crystalline V₂O₅ clusters. A final remark should be made about the formation of mixed metal oxides upon heating of supported vanadium oxide catalysts. It has been shown that MgV₂O₇ and ZrV₂O₇ can be formed when V/MgO and V/ZrO₂ catalysts, respectively are calcined in air [190–193].

5.3. Catalyst activation

The reduction of supported vanadium oxide catalysts at high temperatures in the presence of, e.g. CO and H₂ may lead to the formation of a variety of oxidation states (i.e. V⁵⁺, V⁴⁺ and V³⁺) and coordination

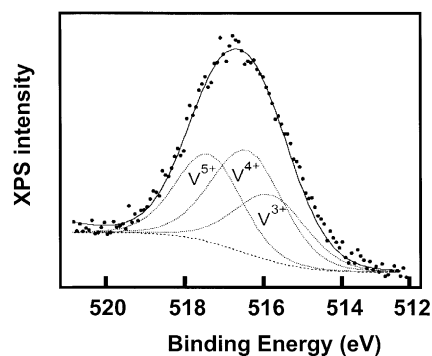


Fig. 8. XPS spectra showing the V 2p_{3/2} region for a 5 wt.% V/Al₂O₃ catalyst reduced at 580 °C for 30 min in CO, including the peak deconvolution for supported V⁵⁺, V⁴⁺ and V³⁺ species.

environments (i.e. VO₄, VO₅ and VO₆) [193]. Many authors have determined the average oxidation state of supported vanadium oxides after reduction with temperature programmed reduction (TPR) techniques, mainly H₂-TPR techniques [194,195]. However, not much is already known about the quantitative distribution of the different vanadium oxide oxidation states (% V⁵⁺, % V⁴⁺ and % V³⁺) and their exact coordination environment at the catalyst surface after reduction and the parameters influencing the reduction degree of supported vanadium oxides. Thus, much more research efforts should be directed towards the elucidation of supported vanadium oxides under reduced conditions.

A possible spectroscopic technique for estimating the amount of V⁵⁺, V⁴⁺ and V³⁺ is XPS. Fig. 8 shows a typical XPS spectrum of a reduced 5 wt.% V/Al₂O₃ catalyst treated at 580 °C for 30 min in CO, together with the proposed peak deconvolutions for the three oxidation states as measured by Harlin et al. [196]. Table 6 summarizes the fractions of V⁵⁺, V⁴⁺ and V³⁺ present in such catalyst after reduction with CO, H₂ and CH₄. It can be seen that the fractions of V⁵⁺, V⁴⁺ and V³⁺ were slightly different after reduction with the different reducing gases and the lowest average oxidation state (3.8) is observed with H₂. Although Eberhardt et al. [97] observed only the presence of V⁵⁺ and V³⁺ on the surface after reduction with H₂ or CO, it has often been concluded that the alumina support also stabilizes reduced V⁴⁺ species. The presence of V⁴⁺ species have indeed been measured by many authors for supported vanadium oxides on alumina by

Table 6

Results of peak deconvolution of the vanadium photoelectron signal after calcination of a 5 wt.% V/Al₂O₃ catalyst in air and after reduction with H₂, CO and CH₄ at 580 °C for 30 min, together with average oxidation states calculated from these fractions [193,196]

Treatment	% V ⁵⁺	% V ⁴⁺	% V ³⁺	Average oxidation state of V
Calcination	100	0	0	5
Reduction with H ₂	21	37	42	3.8
Reduction with CO	34	28	38	4.0
Reduction with CH ₄	32	41	27	4.1

ESR [87–96]. As an example, the ESR spectra of the same 5 wt.% V/Al₂O₃ catalyst after calcination and reduction with CO and H₂ is shown in Fig. 9 [197]. The ESR spectra are typical for an isolated vanadyl species in a pseudo-octahedral coordination. The amount of V⁴⁺ increases in the order: calcined catalyst (8%) < reduced catalyst with CO (13%) < reduced catalyst with H₂ (35%) and this trend is in line with the XPS results presented in Table 6. The exact numbers are not identical most probably due to the introduction of errors in data treatment (e.g. baseline correction).

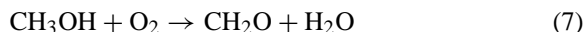
Detailed analysis of the ESR spectra, in combination with spectrum simulation, also revealed that two distinct magnetically isolated V⁴⁺ species can be detected, labeled as species A and B. Both species have similar *g*- and *A*-values indicating two V⁴⁺ species in a slightly different octahedral coordination environment at the catalyst surface. Species A, which is the domi-

nant species after calcination, was almost absent after reduction with H₂ at 580 °C, but a significant amount of species A was always present with CO as the reducing agent, even after reduction at 580 °C. Further characterization studies should now be directed in the elucidation of the coordination environment of species A and B.

5.4. Catalytic operation

Although many reactions can be catalyzed by supported vanadium oxide catalysts, the selective oxidation of methanol to formaldehyde is a particularly useful example because this catalytic reaction can be considered as a simple probe reaction for a number of other selective oxidation reactions [198]. Examples of such oxidation reactions are the selective oxidation of butane to maleic anhydride and *o*-xylene to phthalic anhydride and the oxidative dehydrogenation of alkanes to the corresponding alkenes. As a consequence, the concepts developed for the selective oxidation of methanol over supported vanadium oxide catalysts can be easily transferred to these catalytic reactions as well.

The selective oxidation of methanol can be written as



This reaction is usually conducted at 230 °C in a fixed-bed reactor. During the oxidation of methanol to formaldehyde, the supported vanadium oxides

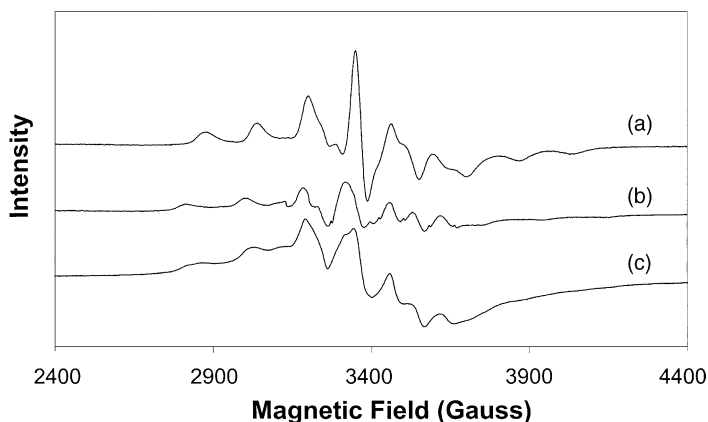


Fig. 9. ESR spectra of a 5 wt.% V/Al₂O₃ catalyst calcined at 580 °C (a), reduced at 580 °C for 30 min in CO (b) and reduced at 580 °C for 30 min in H₂ (c).

become partially reduced by the reaction environment [183,188]. The extent of reduction during methanol oxidation is rather limited and almost independent of the surface vanadium oxide loading, the specific support and the reaction temperature. This suggests that the fraction of supported vanadium(V) oxides is almost constant. In addition, IR spectroscopy reveals the presence of surface methoxy intermediates.

Catalytic measurements show that the selectivities to formaldehyde are 90–99% for V/TiO₂, V/ZrO₂, V/Nb₂O₅ and V/CeO₂, whereas only a selectivity of 50% to formaldehyde was observed for V/Al₂O₃ catalysts [199]. The major unselective product was dimethylether, which is associated with the presence of some surface acid sites at the catalyst surface. The relative independence of the turnover frequency (TOF), which is defined as the number of methanol molecules converted per surface vanadium oxide site per second, with the vanadium oxide loading at each of the amorphous supports, indicates that the reaction rate is first order with respect to the surface vanadium oxide sites. This suggests that the selective oxidation of methanol to formaldehyde over supported vanadium oxide catalysts is a uni-molecular reaction requiring only one surface vanadium oxide species, which can be referred to as the catalytically active site. A possible reaction mechanism is given in Fig. 10, showing the presence of a spectroscopically observed reaction intermediate, namely V–O–CH₃ species [183]. It shows a four-step process, in which first the methanol is chemisorbed onto

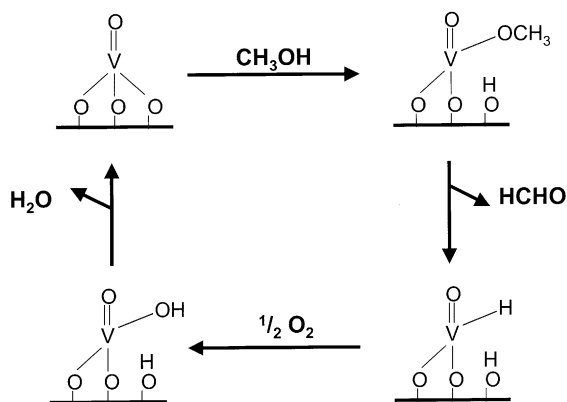


Fig. 10. Reaction mechanism for the selective oxidation of methanol to formaldehyde over supported vanadium oxide catalysts.

the surface vanadium oxide species with the formation of a methoxy group. In the second step, the C–H bond in the adsorbed methoxy group is broken and formaldehyde is released. The breaking of the C–H in the V–O–CH₃ unit is the rate-determining step in the oxidation of methanol to formaldehyde. The third reaction step is the re-oxidation of the reduced vanadium site to V⁵⁺ followed by the release of water. Such scheme is a typical example of the Mars–Van Krevelen redox mechanism, in which the oxidation of hydrocarbons proceeds by a reduction of an oxidized surface site, which is subsequently re-oxidized with gas-phase molecular oxygen.

One of the intriguing questions for years is which molecular bond in the supported vanadium oxides is responsible for the oxidation activity in various catalytic oxidation reactions [200–202]. Three types of bonds can be distinguished: terminal V=O bonds, bridging V–O–V bonds, and V–O–support bonds (Fig. 11). In what follows, we discuss the experimental evidence currently available to evaluate the possible role of each of these bonds in the selective oxidation of methanol.

5.4.1. Role of terminal V=O bonds

Many investigators have been convinced that this bond contains the oxygen critical for methanol oxidation. However, in situ Raman spectroscopy in combination with catalytic measurements has shown that there is no relation between the terminal V=O bonds and the catalytic performances of supported vanadium oxide catalysts. Indeed, the TOF was found to vary drastically, although almost identical V=O Raman features were observed for these catalysts. This is shown in Table 7 and similar results are obtained for the

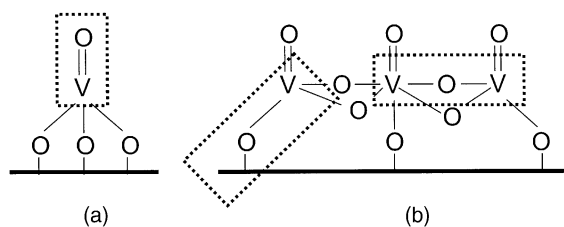


Fig. 11. Three possible V–O bonds involved in the selective oxidation of methanol to formaldehyde: (a) monomeric VO₄ species and (b) polymeric VO₄ species characterized by V=O, V–O–V and V–O–support bonds.

Table 7

Catalytic performances in the selective oxidation of methanol to formaldehyde at 230 °C and Raman frequency of the V=O bond for a series of supported vanadium oxide catalysts [183,188,199]

Supported vanadium oxide catalyst	TOF at 230 °C	V=O bond (cm ⁻¹)
V/SiO ₂	3×10^{-3}	1039
V/Al ₂ O ₃	7×10^{-2}	1026
V/Nb ₂ O ₅	4.5×10^{-1}	1033
V/TiO ₂	1.1×10^0	1030
V/ZrO ₂	1.8×10^0	1030

oxidation of butane to maleic anhydride and the oxidative dehydrogenation of alkanes to alkenes. Furthermore, oxygen-18 labeling of the terminal V=O bond during methanol oxidation revealed that this bond is very stable and has an exchange time that is approximately 20 times longer than the characteristic reaction time. A series of in situ Raman spectra at different degrees of oxygen-18 labeling is given in Fig. 12. It is shown that the V=¹⁸O bond is gradually transformed into a V=¹⁶O bond during methanol

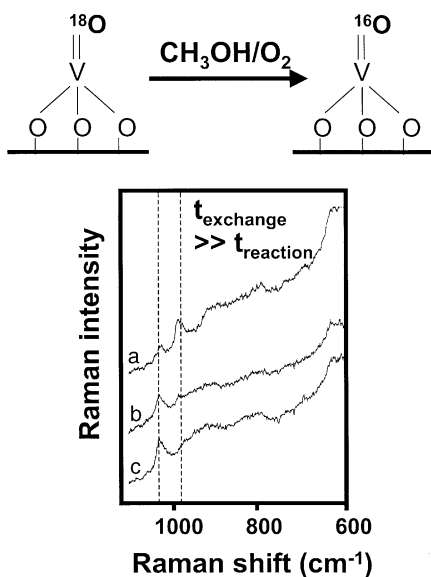


Fig. 12. In situ Raman spectra obtained during the selective oxidation of methanol to formaldehyde over a V/ZrO₂ catalyst. The supported metal oxide catalyst was first partially transformed with ¹⁸O₂ in its ¹⁸O form by a reduction–re-oxidation treatment with *n*-butane and oxygen-18. Repeating this reduction–re-oxidation cycle for several times results in a shift of the 1030 cm⁻¹ Raman band to approximately 1000 cm⁻¹. The 1030 cm⁻¹ is a typical Raman frequency for the V=¹⁶O bond.

oxidation, but with an exchange rate much slower than the effective reaction rate. All these experimental observations strongly indicate that the terminal V=O bonds do not contain the critical oxygen that is involved in the oxidation of methanol to formaldehyde.

5.4.2. Role of bridging V–O–V bonds

It is already discussed that the ratio of polymerized to isolated supported vanadium oxide species increases with increasing vanadium oxide loading (Fig. 7). As a consequence, the surface concentration of bridging V–O–V bonds increases with increasing vanadium oxide loading. The TOF of these catalysts, however, is independent of the vanadium oxide loading, as is illustrated in Fig. 13. This suggests that the oxygen associated with the V–O–V bond does not critically participate in the oxidation of methanol to formaldehyde.

5.4.3. Role of V–O–support bonds

Indirect evidence for the role of this bond can be found by changing the specific support composition. Since changing the specific support oxide composition dramatically influences the TOF of the corresponding supported vanadium oxide catalysts for the selective oxidation of methanol to formaldehyde (Table 7), it strongly suggests that the oxygen in the V–O–support bond is critical for this catalytic oxidation reaction. This observed trend in TOF is a nice example of the metal oxide–support effect in heterogeneous catalysis and by a careful choice of the support oxide one can tune the catalyst performances. More experimental evidence for the role of

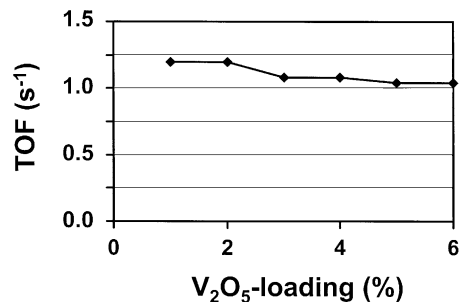
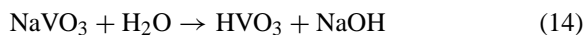
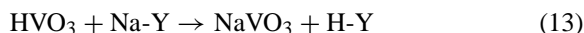
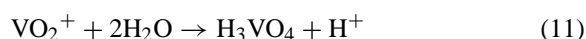
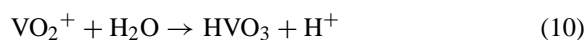
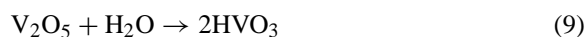
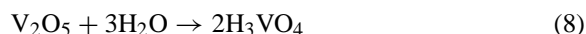


Fig. 13. TOF values of a V/ZrO₂ catalyst as a function of the supported vanadium oxide loading in the selective oxidation of methanol to formaldehyde at 230 °C.

the V–O–support bond in methanol oxidation is difficult since this bond cannot be directly assessed by, e.g. vibrational spectroscopies. However, XAFS spectroscopy, more specifically the XANES technique, allows probing the electronic density on the vanadium in supported vanadium oxide catalysts as a function of the support oxide [203]. It was found that the electron density on vanadium increases in the order: $V/SiO_2 \ll V/Al_2O_3 \ll V/ZrO_2 < V/Nb_2O_5$. This trend was also in line with quantitative measurements of V^{4+} by using the ESR technique. Thus, an increase in electron density as measured with XANES resulted in a decrease in the amount of ESR-visible V^{4+} and an increase in the TOF for methanol in the oxidation to formaldehyde (Table 7). The high electron density of the vanadium facilitates the rate-determining bond breaking step in the V–O–CH₃ reaction intermediate during methanol oxidation.

5.5. Catalyst deactivation

An example in which vanadium oxides play a crucial role in catalyst deactivation is the fluid catalytic cracking (FCC) of crude oil over ultrastable Y (USY) zeolites. A large amount of research has focused on understanding the destructive role of vanadium since it is major issue for catalyst performance during the cracking of residuum-containing feeds [204–209]. It has been shown that the destruction of zeolite Y in the presence of steam occurs via two pathways [209]. The first route is the steam hydrolysis of framework aluminum, while the second route is a direct attack of the Si–O–Si framework by sodium species. Sodium reacts with steam to form an active center, a surface NaOH, which is able to destroy the zeolite structure. The detrimental role of vanadium is now to enhance this second route by acting as a catalyst for the removal of sodium ions from zeolite Y. This could occur according to the following reaction steps:



V–porphyrin or other organic vanadium compounds present in crude oil are oxidized and broken down in the catalyst regenerator, and the released vanadium will migrate at the outer surface of the zeolite since V_2O_5 is a liquid at the reaction conditions. It will react with steam to give acidic compounds (reactions (8) and (9)). Similarly, vanadium can be present as an adsorbed surface species of the form VO_2^+ and can react with steam to form acids (reactions (10) and (11)). The metavanadic acid reacts with the sodium cation of zeolite Y (Na-Y) to form sodium metavanadate (reaction (13)). This sodium metavanadate hydrolyses further to give NaOH and metavanadic acid (reaction (14)). Metavanadic acid can then react again with the zeolite to form sodium metavanadate (reaction (13)). It is clear that metavanadic acid can be considered as a catalyst that facilitates the removal of sodium ions from zeolite Y and this results in the formation of NaOH, which is quite potent for zeolite Y destruction.

A way to prevent this destruction process by supported vanadium oxides is to trap the vanadium compounds, in particular metavanadic acid, onto an oxide coating, which surrounds the zeolite material. This implies insight in the adsorption properties of supported vanadium oxides. In a recent study, the preferential adsorption of $V^{4+/5+}$ ions on SiO_2 , Al_2O_3 and USY has been studied with combined DRS–ESR spectroscopies in quite detail [210]. By taking the spectroscopic fingerprints of $V^{4+/5+}$ on these supports as reference spectra it was possible to monitor the preferential adsorption of $V^{4+/5+}$ onto physical mixtures of these oxides. It was shown that both V^{4+} and V^{5+} ions were preferentially adsorbed on Al_2O_3 and showed a much smaller preference for USY and SiO_2 . Based on this observation, a novel method was developed to coat the external surface of USY with a thin film of Al_2O_3 [210,211]. This method is based on the deposition of USY with the so-called Keggin ion, $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$, which is too big to enter the USY channels or pores. The obtained Al_2O_3 /USY material showed a preferential adsorption of V^{4+} onto the Al_2O_3 film. XPS revealed that all the coated USY materials have a substantial enrichment in the aluminum oxide content in the near-surface region of the zeolite material, while IR spectroscopy proved that the

acidic hydroxyl groups of the zeolite remained intact for cracking reactions. Thus, this coating method could be useful for vanadium passivation in FCC catalysis.

6. Concluding remarks and look into the future

Supported vanadium oxide catalysts are very complex inorganic materials that play an important role in heterogeneous catalysis in both the gas and the liquid phase. Their synthesis and molecular design require a profound knowledge of solution chemistry, solid-state chemistry and inorganic chemistry, and their application as catalysts results from the specific interaction between the support oxide and the vanadium oxide. Insight into the preparation of supported vanadium oxide catalysts at a molecular level would be very beneficial. It is hoped that this goal can be achieved in the future by applying in situ spectroscopic techniques and appropriate spectroscopic reaction cells.

It is also evident that the support characteristics (e.g. chemical composition) have a tremendous impact on the properties of the supported vanadium oxide species. This metal oxide–support effect—in the hydrated state, dehydrated state as well under reaction conditions—is not well studied and therefore not well understood both at a molecular and electronic level. Up to now, no consistent model can describe—in a quantitative manner—the role of the structure/composition of support oxides and the presence of specific promoter elements on the electronic structure of the supported vanadium oxides. This lack of knowledge prevents a rational design of supported vanadium oxide catalysts. Therefore, further research has to be directed towards the use of an intelligent combination of preferably in situ spectroscopic techniques delivering both molecular and electronic information about the supported vanadium oxides. Theoretical calculations of relevant cluster models of supported vanadium oxide catalysts can be in this respect very helpful.

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