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Preface

With advances in the area of metal oxide systems progressing sharply over the past decade, there has been an increasing need for comprehensive surveys and texts that can serve both as introductions for newcomers to the field and as reference materials for the already established investigator. There is no doubt that this timely and interdisciplinary work will emerge as an important milestone and will make a significant impact.

Metal oxides belong to a class of widely used catalysts. They exhibit acidic or basic properties, which make them appropriate systems to be used as supports for highly dispersed metal catalysts or as precursors of a metal phase or sulfide, chloride, etc. Simple metal oxides range from essentially ionic compounds with the electropositive elements to covalent compounds with the nonmetals. However, taking into account the large variety of metal oxides, the principal objective of this book is to examine only metal oxides that are more attractive from the catalytic point of view, and most specifically transition metal oxides (TMO). In particular, TMO usually exhibit nonstoichiometry as a consequence of the presence of defective structures. The interaction of TMO with surfaces of the appropriate carriers develop monolayer structures of these oxides. The crystal and electronic structure, stoichiometry and composition, redox properties, acid—base character and cation valence sates are major ingredients of the chemistry investigated in the first part of the book. New approaches to the preparation of ordered TMO with extended structure of texturally well defined systems are also included.

The second part of the book compiles some practical aspects of metal oxides, with emphasis in catalytic applications. Metal oxides represent an expanding class of compounds with a wide range applications in several areas such as materials science and catalysis, chemical sensing, microelectronics, nanotechnology, environmental decontamination, analytical chemistry, solid-state chemistry, and fuel cells. Our basic knowledge on the metal oxide chemistry is relatively far from that for metals, and as yet, little is known about fundamental relationships between reactivity of oxide compounds and their chemical compositions, crystal structures, and electronic properties at the surface. When examining the importance of metal oxides, and specifically TMOs, in several reactions such as dehydration, selective oxidations, olefin metathesis, VOCs removal, photocatalysis, water splitting, and electrocatalysis, attempts will be made in order to connect properties of the oxides and their reactivity. Since the catalytic phenomenon is confined to the external surface of the solids where molecules or atoms interact, the study of this interaction requires contributions from inorganic and physical chemistry, solid-state chemistry, quantum chemistry, surface science, reaction kinetics, and other branches of science.

In summary, each chapter begins with an excellent introduction to the topic concerned, which is followed by a good overview of the subject and more details for the expert in the area. The book is intended to be used mainly as a research monograph by a vast community of those working in the field of catalysis. However, it may also serve as a supplementary text for postgraduate students working in the fields of industrial chemistry, catalysis, chemical technology, and physical as well as in general chemistry.

Editor

J.L.G. Fierro is a senior research scientist and professor at the Institute of Catalysis and Petrochemistry of the National Council for Scientific Research (CSIC), Madrid, Spain. He is the editor of seven books and the author and coauthor of 600 professional papers, most of which concerned his research on metal oxides, including their synthesis, characterization, and application in catalytic reactions. He is a member of the Spanish Society of Chemistry and the Petroleum Division of the American Chemical Society. Professor Fierro received the B.S. (1973) in chemistry from the University of Oviedo, Spain, and a doctorate (1976) in chemistry from the Complutense University of Madrid.

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1 Molecular Structures of Surface Metal Oxide Species: Nature of Catalytic Active Sites in Mixed Metal Oxides

Israel E. Wachs

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1.1 Introduction

Metal oxide catalytic materials currently find wide application in the petroleum, chemical, and environmental industries, and their uses have significantly expanded since the mid-20th century (especially in environmental applications) [1,2]. Bulk mixed metal oxides are extensively employed by the chemical industries as selective oxidation catalysts in the synthesis of chemical intermediates. Supported metal oxides are also used as selective oxidation catalysts by the chemical industry, as environmental catalysts, to selectively transform undesirable pollutants to nonnoxious forms, and as components of catalysts employed by the petroleum industry. Zeolite and molecular sieve catalytic materials are employed as solid acid catalysts in the petroleum industry and as aqueous selective oxidation catalysts in the chemical industry, respectively. Zeolites and molecular sieves are also employed as sorbents for separation of gases and to trap toxic impurities that may be present in water supplies. Significant molecular spectroscopic advances in recent years have finally allowed the nature of the active surface sites present in these different metal oxide catalytic materials to be determined in different environments. This chapter examines our current state of knowledge of the molecular structures of the active surface metal oxide species present in metal oxide catalysts and the influence of different environments upon the structures of these catalytic active sites.

1.2 Supported Metal Oxides

Supported vanadium oxide catalysts are employed as catalysts for o-xylene oxidation to phthalic anhydride [3], ammoxidation of pyridine to picoline [4,5], methanol oxidation to formaldehyde [6], methane oxidation to formaldehyde [7], ethane oxidative dehydrogenation (ODH) to ethylene [8], propane ODH to propylene [9,10] *n*-butane oxidation to maleic anhydride [11], SO₂ oxidation to SO₃ [12], and oxidesulfurization (ODS) of organosulfur compounds [13-15]. Supported vanadium oxide-tungsten oxide and supported vanadium oxidemolybdenum oxide catalysts are extensively employed as catalysts for the selective catalytic reduction (SCR) of NO_x with NH₃ to N₂ and H₂O [16–18]. Supported tungsten oxide and sulfated catalysts are efficient solid acid catalysts for hydrocarbon isomerization reactions [19-22]. Supported rhenium oxide and tungsten oxide find application as olefin metathesis catalysts [23,24]. Supported chromium oxide, vanadium oxide, and molybdenum oxide catalysts are employed to catalyze olefin polymerization reactions [25-27], of there, supported chromium oxide catalysts are commercially employed as alkane dehydrogenation catalysts [28]. Supported molybdenum oxide and tungsten oxide are precursors to their corresponding sulfides that are formed during hydrodesulfurization (HDS) of organosulfur compounds [29,30]. Thus, the applications of supported metal oxide catalysts have significantly expanded since their first applications in the mid-20th century.

It is important to know the molecular structures of the active sites present in supported metal oxide catalysts in order to fully understand their fundamental characteristics. Supported metal oxide catalysts consist of an active metal oxide phase dispersed on a high surface area oxide support [2,31]. The dispersed metal oxide active phase is typically present as a two-dimensional metal oxide overlayer on the high surface area oxide substrate. The molecular structures of the surface metal oxide species have been found to be different than their pure metal oxide phases [31]. For example, supported VO_x possesses VO₄ coordination and bulk V₂O₅ consists of distorted VO₅ coordination [32,33]. Furthermore, the molecular structures of the surface metal oxide species are *dynamic* and strongly depend on the specific environment (e.g., gas phase composition, temperature, and pressure). This portion of the chapter will review what is currently known about the molecular structures of the surface metal oxide species present in supported metal oxide catalysts and the influence of different environments on the structures. Subsequent sections of this chapter will show how these findings can be extended to other mixed metal oxide catalytic materials.

1.2.1 Hydrated Surface Metal Oxide Species

Supported metal oxide species are hydrated when exposed to moist environments and low temperatures ($<230^{\circ}$ C). Thus, all calcined supported metal oxide species are hydrated at ambient conditions (room temperature and air exposed) [34,35]. The hydrated surface layer corresponds to a thin aqueous film that corresponds to multiple layers of moisture [32]. The hydrated surface metal oxide species equilibrate with the pH of the aqueous layer. The pH of the aqueous film is determined by the pH at point zero charge (PZC) of the hydrated surface [36,37]. The net pH at PZC is defined as the equilibrated pH of a hydrated surface when the net charge is zero (protonated positive surface sites are balanced by an equal number of deprotonated negative surface sites). At pH values above the PCZ, the hydrated surface becomes negatively charged, while for pH values below the PCZ, the hydrated surface becomes positively charged. Thus, hydrated surfaces always equilibrate at the pH at PZC in order to preserve charge balance.

The net pH at PZC for a supported metal oxide catalyst possessing monolayer surface coverage is dependent on the pH at PZC value of the oxide support substrate and the pH at PZC value of the pure metal oxide that is in the dispersed metal oxide phase:

pH at
$$PZC_1$$
(monolayer) ~ ($PZC_{support} + PZC_{dispersed oxide}$)/2 (1.1)

Both the oxide support and the dispersed oxide exert an influence on the net pH at PZC because the thin aqueous film is in contact with both components (especially when clusters of the surface metal oxides are present). Below monolayer surface coverage, the pH at PZC is a function of the surface coverage of the dispersed oxide and monotonically decreases from the value of the oxide support to the value at monolayer coverage given by Equation (1.1) with increasing surface coverage. The individual values of the pH at PZC for pure oxides at room temperature are well documented in the literature [36–38] and are presented in Table 1.1 for typical oxides encountered as oxide supports and active metal oxide phases.

Support	pH at PZC	Active surface oxide	pH at PZC		
MgO	12.4	V_2O_5	1.4		
γ -Al ₂ O ₃	8.8	Nb_2O_5	4.3		
CeO ₂	6.8	CrO ₃ (Cr ₂ O ₃)	ws (7.0)		
ZrO ₂	6.7	Ta ₂ O ₅	~ 4		
TiO ₂	6.3	MoO ₃	1.2		
Nb ₂ O ₅	4.3	WO ₃	0.7		
SiO ₂	1.8	Re ₂ O ₇	WS		

TABLE 1.1pH at PZC for Oxide Supports and Active SurfaceMetal Oxides

ws - water soluble metal oxide.



FIGURE 1.1 The influence of the surface coverage of different surface metal oxides on the net pH at PZC for a series of Al_2O_3 supported metal oxides

The influence of the surface coverage of different surface metal oxides on the net pH at PZC for a series of Al_2O_3 supported metal oxides is shown in Figure 1.1. The pH at PZC of the Al_2O_3 support is ~8.8 and continuously decreases as the surface coverage of metal oxides with low values of pH at PZC is increased. Note that at monolayer surface coverage the net pH at PZC of the different supported metal oxide catalysts asymptotically reaches values intermediate between that of the pure alumina support and the pure dispersed metal oxide phase.

The molecular structures of hydrated metal oxide species in aqueous solution are well documented and depend on the solution pH and the metal oxide aqueous concentration with the solution pH having the dominant effect [39]. For high pH values, the hydrated metal oxides tend to be present as isolated MO₄ units in



FIGURE 1.2 The V⁺⁵ aqueous phase diagram

solution (e.g., VO₄, CrO₄, MoO₄, WO₄, ReO₄, etc.). For low pH values, the hydrated metal oxides tend to be present as linear polymeric chains (e.g., $(CrO_3)_n$ with *n* equal to 2 or greater) and clusters (e.g., $V_{10}O_{28}$, Mo₇O₂₆, Nb₆O₁₉, Ta₆O₁₉, W₁₂O₃₉). One exception to this trend is aqueous rhenium oxide that is present as isolated ReO₄ species at all pH values and concentrations. The aqueous phase diagram of vanadium oxide is shown in Figure 1.2. The vanadium oxide molecular structure is very sensitive to the aqueous pH and forms VO₄ (orthovanadate), V₂O₇ (pyrovanadate), V₃O₁₀ (trimer), V₄O₁₃ (metavanadate or tetramer), V₁₀O₂₈ (decavanadate), and V₂O₅. *n*H₂O (V₂O₅ gel) complexes.

The molecular structures of the hydrated surface metal oxides on oxide supports have been determined in recent years with various spectroscopic characterization methods (Raman [34,37,40–43], IR [43], UV-Vis [44,45], solid state NMR [32,33], and EXAFS/XANES [46–51]). These studies found that the surface metal oxide species possess the same molecular structures that are present in aqueous solution at the same net pH values. The effects of vanadia surface coverage and the different oxide supports on the hydrated surface vanadia molecular structures are shown in Table 1.2. As the value of the pH at PZC of the oxide support decreases, the hydrated surface vanadia coverage increases, which decreases the net pH at PZC, the hydrated surface vanadia species also become more polymerized and clustered. Consequently, only the value of the net pH at PZC of a given hydrated supported metal oxide system is needed to predict the hydrated molecular structure(s) of the surface metal oxide species.

The finding that only one parameter, the net pH at PZC, controls the hydrated molecular structures of surface metal oxide species also has very

,		0	
		Observed mole	cular structures
Oxide support	pH at PZC	Low surface coverage	High surface coverage
MgO	12.4	VO_4 , V_2O_7 , $(VO_3)_n$	$VO_4, V_2O_7, (VO_3)_n$
Al_2O_3	8.8	$(VO_3)_n$	$(VO_3)_n, V_{10}O_{28}$
ZrO ₂	6.7	V_2O_7 , $(VO_3)_n$, $V_{10}O_{28}$	$V_{10}O_{28}$
TiO ₂	6.3	$(VO_3)_n, V_{10}O_{28}$	$V_{10}O_{28}$
SiO ₂	1.8	V2O5.nH2O	V2O5

TABLE 1.2Hydrated Molecular Structures for Supported Vanadium OxideCatalysts as a Function of Surface Coverage and Specific Support

important implications for the synthesis of supported metal oxide catalysts since all preparation methods, for a given composition and catalyst system, must equilibrate at the same net pH at PZC upon hydration. This means that the preparation method cannot influence the final hydrated, as well as the subsequent dehydrated, surface metal oxide molecular structures. This has been demonstrated for various supported MoO₃/TiO₂ [52], MoO₃/SiO₂ [53], and V₂O₅/TiO₂ [52] catalytic systems synthesized with different precursors and sources of oxide supports. Furthermore, the specific phase of the oxide support (e.g., TiO₂ [anatase], TiO₂ [rutile], TiO₂ [brookite], and TiO₂ [B]) also did not affect the hydrated molecular structures of the surface metal oxide species for the same surface metal oxide coverage [54]. The series of samples examined in these studies originated in many different catalysis laboratories around the world and confirmed that the hydrated molecular structures are independent of the origin of the supported metal oxide catalysts. These conclusions are further confirmed by a careful examination of the catalysis literature containing reproducible structural characterization information of supported metal oxide species.

The only different molecular structures were found for supported metal oxide catalysts where the oxide support contained surface impurities such as Ca [55], Na [55,56], Ca [53,56], and K [34,56]. These basic impurities alter the hydrated molecular structures by increasing the net pH at PZC on the thin aqueous film or directly reacting with the surface metal oxide species to form nanocrystalline compounds (e.g., CaMoO₄, Na₂MoO₄, K₂MoO₄, etc.). The presence of nanocrystalline metal oxide species *below monolayer surface coverage* typically results from preparations employing precursors that have limited or low solubility in the impregnating solvents (e.g., NH₄VO₃ in water, V₂O₅ in aqueous oxalic acid solution). In such instances, the metal oxide precursors are not well dispersed over the oxide support surface and tend to form the crystalline metal oxide phases upon calcination. For some supported metal oxide systems, it was observed that the surface metal oxide were initially able to form hydrated complexes with the oxide

support cations (e.g., silicomolybdic acid [57] and AlMo₆O_x clusters [58,59]) for specific preparation sequences, but such hydrated clusters are not stable at 300°C and higher temperatures owing to the loss of waters of hydration, and decompose during calcination to the conventional surface metal oxide species. Thus, the final hydrated supported metal oxide catalysts *after calcination* have no memory effect of the prior presence of such hydrated complexes with the oxide support since they decompose during calcination.

As the supported metal oxide catalyst temperature is increased, the thin aqueous film evaporates and desorbs, ~ 100 to 200° C, from oxide surfaces to yield dehydrated surfaces. If sufficient moisture is present in the environment at the elevated temperatures, however, it is still possible to maintain an extensively hydrated surface up to $\sim 230^{\circ}$ C [35]. At higher temperatures, the desorption rate of the adsorbed moisture from oxide surfaces is very fast and the surfaces are essentially dehydrated (<5% of the surface contains adsorbed moisture at steady-state when moisture is present) [35].

1.2.2 Dehydrated Surface Metal Oxide Species

The dehydrated surface metal oxide species are not coordinated to water and, therefore, their molecular structures are not related to those present in aqueous solutions. Consequently, the pH at PZC model cannot be employed to predict the dehydrated surface metal oxide structures. The molecular structures of the dehydrated surface metal oxide species, however, possess similarity to the structural inorganic chemistry of bulk metal oxides because of the absence of water ligands in both systems [60–62]. Instead of being solvated by coordinated water in the aqueous solution complexes, the bulk metal oxide structures are coordinated to various cations (e.g., K, Na, Ca, Mg, Fe, Al, Ce, Zr, Ti, etc.). Prior to discussing the current understanding of the molecular structures of the dehydrated surface metal oxide species, a brief review of the structural inorganic chemistry of bulk metal oxides are presented to highlight the molecular structural similarities, as well as differences, between these two- and three-dimensional metal oxide systems.

1.2.2.1 Structural determination methods

The bulk metal oxide structures have been determined with extensive and highly accurate x-ray diffraction crystallographic studies [60]. Unfortunately, the structural inorganic chemistry of dehydrated surface metal oxides on oxide supports cannot be determined with x-ray diffraction crystallography because of the absence of long-range order (>4 nm) in the surface metal oxide overalyers. Information about the local structures of the dehydrated surface metal oxides, however, can be obtained with *in situ* molecular spectroscopic techniques of dehydrated supported metal oxides: Raman [31,63], IR [64], UV-Vis [44,50,65,66], XANES/EXAFS [46–51,67,68], chemiluminescence [69], and solid state NMR for certain nuclei (e.g., ⁵¹V, ⁹⁵Mo, ¹H, etc.) [32,33,70,71]. UV-Vis, XANES/EXAFS,

chemiluminescence, and solid state NMR provide structural details about the number of O atoms coordinated to a cation (e.g., MO₄, MO₅, or MO₆) and the presence of adjacent neighbors (M–O–M). The bridging M–O–M bonds are also easily detectable with Raman spectroscopy and occasionally also in the IR overtone region. Coupled Raman, IR, and isotopic oxygen exchange studies can establish the number of terminal M=O bonds (e.g., monoxo M=O, dioxo O=M=O or tri- $0 \times 0 = 0$ oxo M(=O)₃) [64]. For isolated mono-oxo units, the M=O symmetric stretch, v_s , appears at the same frequency in both the Raman and IR spectra. In addition, the IR overtone region exhibits only one band at $\sim 2v_s$. For isolated dioxo structures, the O=M=O functionality possesses both symmetric, v_s , and asymmetric, v_{as} , stretching modes that can be separated by about $\sim 10 \text{ cm}^{-1}$ and the IR overtone region exhibits three bands at $\sim 2v_s$, $v_s + v_{as}$, and $\sim 2v_{as}$ that span over a ~ 20 cm⁻¹ range. For isolated trioxo functionalities, the vibrational spectra are more complex and multiple bands will generally be present in the stretching and overtone regions. For dimeric monoxo species, where the M=O bonds are in the cis configuration, the v_s and v_{as} stretching modes are separated by ~10 to 50 cm⁻¹ and a triplet of bands is also present in the overtone region. For dioxo dimers, the stretching modes are separated by more than 50 cm⁻¹. For polymeric monoxo and polymeric dioxo species, the fundamental stretching vibrations are not coincident and the overtone region reflects the multiplicity of the fundamental stretching vibrations. Raman is generally more sensitive to v_s and IR is generally more sensitive to v_{as} . In the event that the O=M=O bonds are separated by at a 90°, then the vibrations will degenerate and the splitting of the bands will not be observed. Isotopic ¹⁶O/¹⁸O exchange studies are able to split such degenerate vibrations by scrambling of the oxygen isotopes. For monoxo structures, two symmetric stretching bands will be present due to $M=^{16}O$ and $M=^{18}O$ vibrations. For dioxo structures, three symmetric stretching bands will appear due to ${}^{16}O=M={}^{16}O, {}^{18}O=M={}^{18}O,$ and ¹⁶O=M=¹⁸O vibrations, and four symmetric stretching bands should appear for trioxo functionalities (M¹⁶O₃, M¹⁸O¹⁶O₂, M¹⁸O¹⁶O₂, and M¹⁸O₃). In addition, the isotopic shifts due to the substitution of the heavier 18 O for 16 O can also be calculated for diatomic oscillators and compared with the observed isotopic shifts [62]. Thus, the combination of these molecular spectroscopic measurements coupled with isotopic oxygen exchange studies are required to obtain the complete dehydrated surface metal oxide structures.

1.2.2.2 Vanadium (+5) oxides

The bulk structural inorganic chemistry of vanadium (+5) oxides is the most varied among the bulk metal oxides, and has been determined from extensive x-ray crystallographic studies [60]. Bulk VO₄ vanadate ions consist of isolated (VO_4^{3-} orthovandate), dimeric ($V_2O_7^{4-}$ pyrovanadate) or polymeric chain (($VO_3)_n^{n-}$ metavanadate) structures. These four-coordinated vanadate ions are distinguished by the number of bridging V–O–V bonds that are present in the orthovanadate (0), pyrovanadate (1), and metavandate (2) structures, and are charge balanced by cations (e.g., Na₃VO₄, Na₄V₂O₇, and Na_n(VO₃)_n). Bulk VO₆

vanadates are also very common structures, and are typically found in extended vanadia structures. For example, the decavandate cluster in Na₆V₁₀O₂₈ consists of five distinct distorted VO₆ sites [72]. The highly distorted VO₆ structures usually possess one terminal V=O bond (monoxo) with bond lengths between 0.158 and 0.162 nm. For some highly distorted VO₆ oxides, the sixth O is located very far from the V atom that these compounds are effectively considered to possess VO₅ coordination. This is the case for bulk V₂O₅ that contains its 6 O atoms at 0.158, 0.178, 0.188, 0.188, 0.202, and 0.278 nm, with the most distant oxygen usually not considered to be in the V coordination sphere. Several gas phase monoxo X₃V=O halide species are also known and their vanadyl vibrations vary from 1025 to 1058 cm⁻¹ with increasing electronegativity of the halides (Br < Cl < F) [61]. The dixo F₂VO₂⁻ and Cl₂VO₂⁻ oxyhalide vibrations are observed at 970/962 and 970/959 cm⁻¹, respectively. In summary, the rich inorganic chemistry of bulk vanadium (+5) oxide is built up from VO₄, VO₅, and VO₆ coordinated structures.

Spectroscopic characterization studies employing solid state ⁵¹V NMR [32,33], XANES/EXAFS [46,47,73], UV-Vis [44], and chemiluminescence [69] have revealed that the dehydrated surface VO_x species consist of highly distorted VO₄ units up to monolayer surface coverage. Above the monolayer surface vanadia coverage, V₂O₅ crystallites, possessing VO₅ coordination, are also present on top of the surface VO_x monolayer. In situ Raman and IR spectroscopic studies have demonstrated that the dehydrated surface VO₄ species possess only one terminal V=O bond [43,64,74] because of the same fundamental vibrational band position detected by both techniques. The dehydrated terminal V=O bond exhibits its fundamental vibration in the 1015 to 1040 cm^{-1} region and its overtone vibration at $\sim 2036 \text{ cm}^{-1}$ [64,74,75]. The fundamental vibration is dependent on the specific oxide support and the surface vanadia coverage. Isotopic oxygen exchange studies, further confirm the presence of only monoxo surface VO₄ species since the V=O band splits into doublets [43,63,76]. The remaining three oxygen atoms are coordinated to the oxide support cation, bridging V-O-S where S represents the support, when the dehydrated VO₄ site is isolated. EXAFS/XANES analysis concluded that the dehydrated surface VO₄ species on SiO₄ is isolated and contains a monoxo vanadyl structure, O-V(-O-Si)₃ [46,77].

For supported V₂O₅/SiO₂, Raman and UV-Vis spectroscopy reveal only the presence of isolated surface VO₄ species with a sharp band at ~1035 cm⁻¹ from the terminal V=O bond of the dehydrated surface VO₄ species [77,78]. The overtone region exhibits a single band at ~2055 cm⁻¹ consistent with a monoxo V=O functionality [79]. The monoxo nature of the V=O bond for the isolated surface VO₄ species on SiO₂ was further confirmed by the splitting of this band into a doublet during isotopic oxygen exchange [80]. The experimentally observed isotopic shift of 43 cm⁻¹ agrees well with the theoretically determined isotopic shift of 45 cm⁻¹ for a diatomic V=O oscillator [76]. The ~1035 cm⁻¹ vibration also falls in the range observed for the vibrations of vanadyls in gas phase monoxo halides (1025 to 1058 cm⁻¹). The low reactivity of the surface Si–OH functionality is responsible for the low surface coverage and isolated nature of surface metal oxides dispersed on the SiO₂ support [81].

For non-SiO₂ supported vanadia catalysts, the simultaneous presence of dehydrated polymeric surface VO₄ species and dehydrated isolated surface VO₄ species is detected by *in situ* UV-Vis as a shift in the $O^{2-} \rightarrow V^{5+}$ charge transfer transition from ~ 250 to ~ 300 nm, as well as a decrease in the band gap energy, E_g , from 3.6 to 2.6 eV [44,82]. In addition, Raman detects vibrations originating from bridging V-O-V bonds at \sim 500-600 (v_s), 700-800 (v_{as}), and 200-300 cm⁻¹ (bending mode) when the oxide support does not obscure these vibrational regions [75,83]. For example, the bridging V–O–V vibrational modes are readily observed on the Al₂O₃ support with Raman spectroscopy [74,75]. For non-SiO₂ supports, the isolated monoxo structure of the dehydrated surface VO₄ species responsible for the $\sim 1030 \text{ cm}^{-1}$ band is confirmed by (1) the coincidence of this band in Raman and IR, (2) splitting of this band into a doublet during isotopic oxygen exchange (both in Raman and IR), (3) the presence of only one band in the IR overtone region, and (4) its vibration falls in the vibrational region of 1025 to 1058 cm^{-1} for monoxo gas phase oxy halides [43,61,76]. The relative concentration of dehydrated polymeric to isolated surface vanadia species generally increases with surface vanadia coverage as reflected in the decrease in the band gap values [44,82]. From in situ UV-Vis spectroscopy it appears that the dehydrated polymeric surface vanadia species on the nonsilica supports probably form extended polymeric $(VO_3)_n$ structures with $n \gg 2$ at monolayer surface coverage because of the low measured $E_{\rm g}$ values [44,82,84].

Weak IR bands due to V=O bonds are also observed at \sim 1015 to 1017 cm⁻¹ at monolayer surface coverage and have been assigned to surface polymeric VO_4 species [74]. This vibrational position is just slightly lower than that for the monoxo vanadyls of the gas phase halides, 1025 to 1058 cm^{-1} , and is consistent with greater delocalization of monoxo V=O electrons over a more extended surface polyvanadate species. The absence of the additional expected multiple bands for surface polymeric monoxo species may be due to their overlap with the much stronger V=O vibration of the isolated surface monoxo VO₄ species. An exception to this general observation, however, is found for the supported V2O5/CeO2 system where IR detects two small shoulders at 1022 and 1029 cm^{-1} that would correspond to polymeric surface VO₄ species [74]. Furthermore, reactivity studies with supported 1% V2O5/CeO2 have shown that the bands for the isolated, $\sim 1030 \text{ cm}^{-1}$, and polymeric species, $\sim 1015 \text{ cm}^{-1}$, do not behave the same and, therefore, must originate from different surface VO₄ species [63]. The band associated with the surface polymeric VO₄ species is selectively, partially reduced in reactive environments. Detailed EXAFS analysis studies were not able to account for the presence of the polymeric surface vanadate species since the spectra could be fitted with only an isolated surface VO₄ species [73]. However, a minor residual component in the EXAFS spectra may be due to the polymeric surface vanadates [73]. Thus, the fraction of polymeric surface VO_4 species in the surface vanadia monolayer may be small because (1) the surface polymeric V=O bond generally does not give rise to strong vibrations relative to the surface isolated monoxo VO₄ species [74], (2) the overtone region only exhibits the V=O vibration from the isolated surface monoxo VO₄ species [64,74,85], and (3) the EXAFS analysis cannot



FIGURE 1.3 Structures of (a) dehydrated isolated and (b) polymeric surface monoxo VO₄ species

account for a minor residual component that may be due to the polymeric surface VO_4 species [73].

The molecular structures of the dehydrated, isolated, and polymeric surface vanadia species are depicted in Figure 1.3. The surface vanadia structural chemistry under dehydrated conditions reflects the known bulk vanadium oxide inorganic chemistry, in that isolated and polymeric VO_4 units form with only monoxo terminal V=O bonds.

Although monoxo isolated and dimeric VO₄ bulk structures are known [33], polymeric monoxo VO₄ bulk structures have not been reported in the literature and appear to be unique to the dehydrated surface vanadia structures.

1.2.2.3 Chromium (+6) oxides

Bulk chromates possess CrO₄ coordination in isolated (CrO₄ monochromate), dimer (Cr_2O_7 dichromate), trimer (Cr_3O_{10} trichromate), and tetramer (Cr_4O_{13} tetrachromate) infinite chain (CrO₃ metachromate or polychromate) structures [60]. Unlike the corresponding bulk vanadates, bulk non-CrO₄ containing structures are unknown (e.g., CrO_5 and CrO_6). The crystalline CrO_3 structure is built up of infinite chains by linking CrO_4 units (two short bonds at 0.160 nm and two longer bonds at 0.175 nm) that are only held together by van der Waal forces. The unusually low melting point of CrO₃, 197°C, reflects the weak van der Waal interactions among the polychromate chains. The low thermal stability of bulk CrO₃ is also reflected in its facile reduction and decomposition to bulk Cr₂O₃, which consists of only Cr(+3) cations [27,61]. The Cr(+6) oxidation state is usually stabilized by the presence of nonreducible cations (e.g., K, Na, Rb, P, and As). Gas phase chromium oxy halides are also known and monoxo F₄Cr=O vibrates at 1028 cm⁻¹, dioxo $F_2Cr(=O)_2$ vibrates at 1006 (v_s) and 1016 (v_{as}) cm⁻¹, dioxo Cl₂Cr(=O)₂ vibrates at $984 (v_s)$ and $994 (v_{as})$ cm⁻¹, and trioxo CsBrCr(=O)₃ vibrates at 908 (v_s), 933 (v_{as}), 947 (v_{as}), and 955 (v_{as}) cm⁻¹ [86]. These vibrational frequency shifts as a function of the M=O bonds are significantly beyond that expected for the different halide ligands since the gas phase vanadyl oxy halide complexes shifted downward 23 cm⁻¹ in going from F to Cl ligands and downward 10 cm^{-1} in going from Cl to Br ligands. Therefore, increasing the number of chromyl bonds shifts the vibrations to lower wave numbers and progressively increases the number of vibrational bands. In summary, the inorganic structural chemistry of Cr(+6) chromates essentially consists of CrO_4 units with different extents of polymerization.

Spectroscopic characterization of the dehydrated supported chromates with UV-Vis [45,65], chemiluminescence [69], and EXAFS/XANES [87] revealed that the dehydrated surface chromates possess CrO₄ coordination and are stabilized as Cr(+6) at elevated temperatures by the oxide supports below monolayer surface coverage. Above the monolayer surface coverage, the excess chromium oxide that resides on the surface chromia monolyer becomes reduced at elevated temperatures in oxidizing environments and forms Cr(+3) Cr_2O_3 crystallites [41,87]. Thus, the surface Cr(+6) species are only stabilized at elevated temperatures by coordination to the oxide substrates. For non-SiO₂ supports, the Raman and the IR vibrational spectra exhibit two strong bands in the fundamental (1005-1010 and $1020-1030 \text{ cm}^{-1}$) as well as the overtone (1986–1995 and 2010–2015 cm⁻¹) vibrational regions. These bands occur at the exact same fundamental vibrations as well as relative intensities in the Raman and the IR spectra of the Al₂O₃, ZrO₂, and TiO₂ supported chromates, and are separated by 15 to 20 cm⁻¹ [88]. The vibrational difference is consistent with dioxo functionality, but is slightly on the high side [64]. However, the Raman and the IR relative intensities of the v_s and v_{as} modes should vary inversely because Raman is more sensitive to symmetric stretches and IR is more sensitive to asymmetric stretches, but the observed band intensities are the same in IR and Raman [64]. Furthermore, the very high position of the Cr-O vibrations is consistent with that of the isolated monoxo chromyl structures, 1028 cm^{-1} , and not of the isolated dioxo chromyl structure, 984 to 994 $\rm cm^{-1}$, present for the isolated gas phase isolated chromium oxyhalides (see earlier). Additional insights were obtained from isotopic oxygen exchange experiments that showed that both bands split into doublets [76]. This reveals that these two bands originate from two independent surface monoxo chromyl species since a single dioxo species would be expected to only give rise to a triplet. This conclusion was further substantiated by reactivity studies that demonstrated that the two surface chromate species reduce at different rates [89-91]. Comparison of the vibrational bands at different extents of reduction revealed that the 1010 cm⁻¹ band decreased in the same ratio as bridging Cr-O-Cr vibrations and, consequently, was assigned to dehydrated surface polychromate species [91]. The reduction extent of the 1030 cm⁻¹ band did not parallel any of the other bands and was, thus, assigned to the isolated monoxo surface chromate [91].

It is not possible to obtain the chromyl vibrations with IR for low surface coverage of chromia because the SiO₂ support absorbs the fundamental and overtone regions for low surface coverage of surface CrO_x on SiO₂ [64,88]. The corresponding Raman spectrum reveals that the dehydrated surface CrO_x species on SiO₂ is isolated since no bridging Cr–O–Cr vibrations were detected [88,91]. The somewhat low Raman vibration of ~986 cm⁻¹ of the supported CrO₃/SiO₂ catalyst suggests (recall that gas phase dioxo Cl₂CrO₂ exhibits Raman vibrations at 984 (v_s) and 994 (v_{as}) cm⁻¹) that it may arise from dioxo surface chromate species and that the two expected vibrations are degenerated. Model sesquoxide (sp???) chromia silica model compounds have been proposed to possess dioxo chromate species [Feher reference]. Only isotopic oxygen exchange studies and comparative Raman and IR characterization studies can clearly discriminate



FIGURE 1.4 Structures of (a) dehydrated isolated and (b) polymeric surface monoxo CrO₄ species

between monoxo and dioxo surface chromate species for the dehydrated supported CrO_3/SiO_2 catalyst, however, such successful studies have not been reported till date in the literature.

The presence of bridging Cr–O–Cr bonds is revealed by the $O^{2-} \rightarrow Cr^{6+}$ ligand to metal charge transfer transition [92] and by Raman vibrations at 770 (v_{as}), 600 (v_s) and bending modes in the 300 to 400 cm⁻¹ range when not obscured by the support vibrations [88]. The expected vibrational band splitting for the polymeric surface monoxo CrO₄ species was not observed and the additional band may overlap the adjacent band of the isolated monoxo CrO₄ species. The bridging Cr–O–Cr vibrations are easily detected on Al₂O₃, and the ratio of polymeric to isolated surface CrO₄ species appears to be relatively constant with surface coverage. No studies have addressed the issue of the fraction of the surface chromate species that are present as polymeric CrO₄ species.

The molecular structures of the dehydrated surface chromate species are schematically presented in Figure 1.4. The dehydrated surface CrO_4 structures have much in common with their corresponding bulk chromates, CrO_4 coordination and different extents of polymerization, but the surface chromates are monoxo, with the possible exception of the SiO₂ support, and the bulk chromates approach dioxo coordination upon extensive polymerization ($n \gg 4$ as in bulk CrO_3). Thus, monoxo chromates are unique to surface chromate species on oxide supports and some gas phase oxyhalides. Furthermore, the oxide supports stabilize the surface chromate species in the Cr(+6) oxidation state, and chromia in excess of monolayer surface coverage becomes reduced to Cr(+3) Cr_2O_3 crystalline particles upon calcination at elevated temperature.

1.2.2.4 Rhenium (+7) oxides

The bulk inorganic chemistry of rhenium (+7) oxides is rather sparse [60,93]. Several ortho-rhenate compounds containing isolated ReO₄ units are rather common: NH₄ReO₄, KReO₄, and NaReO₄. Bulk Re₂O₇ possesses a layered structure consisting of alternating ReO₄ and ReO₆ groups, with subunits of rings composed of two ReO₄ and two ReO₆ groups. The weak bonding between the rhenium oxide units in the layered Re₂O₇ structure results in the efficient vaporization of Re₂O₇ dimers that contain two ReO₄ units bridged by one oxygen atom (gaseous O₃Re–O–ReO₃). The ReO₃ groups in the gas phase Re₂O₇ dimer consist of trioxo terminal Re=O bonds that vibrate at 1009(v_s of terminal Re=O), 972 (v_{as} of terminal Re=O), 456 (v_s of bridging O–Re–O), 341 (bending of
O–Re–O), and 185 cm⁻¹ (bending of bridging Re–O–Re). The expected splitting of the asymmetric vibrations due to the C_{3v} symmetry of the –O–Re(=O)₃ units was not observed because of the degeneracy of these vibrational modes. Trioxo gas phase rhenium oxyhalides of XReO₃ are also known and exhibit the terminal Re=O v_s vibrations at 997 to 1009 cm⁻¹, which increases with the halide electronegativity (Br < Cl < F) [94]. The gas phase dioxo F₃ReO₂ oxyhalide exhibits its terminal Re=O vibrations at 1026 (v_s) and 990 (v_{as}) cm⁻¹ [95] and the monoxo F₅Re=O possesses its terminal Re=O v_s vibration at 990 cm⁻¹ [62]. The lower Re=O v_s vibration of the monoxo F₅Re=O molecule relative to the dioxo F₃ReO₂ is somewhat surprising since the bond order of the M=O terminal functionality generally increases upon decreasing the number of terminally coordinated oxygen atoms (see gas phase chromate oxyhalides). Thus, the rhenium oxide structural inorganic chemistry is composed of isolated ortho-rhenates (ReO₄), ReO₄ dimers (O₃Re–O–ReO₃), and polyrhenates composed of mixtures of alternating ReO₄ and ReO₆ groups.

The maximum attainable surface ReO_x coverage on oxide supports is always less than monolayer coverage because the surface ReO_x species combine to form volatile Re_2O_7 dimers at high surface coverage [42]. Furthermore, crystalline Re_2O_7 is never observed because this metal oxide is not stable to high temperature calcination as well as to exposure to ambient moisture. Consequently, monolayer surface ReO_x coverage is never reached because volatilization and crystalline Re_2O_7 is never present. Thus, supported ReO_x catalysts are unique among the supported metal oxide catalysts in that only surface ReO_x coverage below monolayer can be achieved without the presence of crystallites.

The dehydrated supported ReO_x/Al_2O_3 system has received most attention among the different supported ReO_x catalysts in the literature. The coordination of the dehydrated surface ReO_x species was determined from XANES [51] and UV-Vis [96] to be distorted ReO₄. The complementary Raman and IR spectra revealed that two different dehydrated surface ReO_x species are present in Al₂O₃ with Re=O v_s at ~1015 and ~1004 cm⁻¹ and corresponding Re=O v_{as} at ~980 and 890 cm^{-1} , respectively. The only difference between the two surface ReO₄ species is the slightly different Re-O bond lengths that caused the vibrational shifts. The Raman and IR vibration bands are coincident and the IR overtone region reveals two distinct bands at 1972 and 1994 cm⁻¹, which is consistent with the presence of two different surface ReO₄ species [41,97]. IR isotopic oxygen exchange studies resulted in the shifting of the terminal Re=O vibrations in the overtone region to \sim 1896 cm⁻¹ and the broadness of the resulting band prevented further resolution of the overtone modes [98]. The IR fundamental vibrations also shifted to lower wave numbers due to the heavier mass of the ¹⁸O atom and were masked by the strong IR absorption of the Al₂O₃ support in this lower vibration region [98]. Raman spectroscopy revealed that the surface ReO_{r} species on Al_2O_3 were isolated since no vibrations originating from a bridging Re-O-Re functionality were detected $(v_{\rm s} \sim 456 \text{ and bending} \sim 185 \text{ cm}^{-1})$ and only the expected bending vibrations of O-Re-O functionally were present at 340 cm^{-1} with a shoulder at 310 cm^{-1} [42,97]. The Re=O v_s and v_{as} vibrations of the dehydrated surface ReO₄/Al₂O₃

species on Al₂O₃ are consistent with the vibrations exhibited by trioxo monomeric gas phase oxyhalides XRe(=O)₃, possessing C_{3v} symmetry, at 997-1009 and 963–980 cm⁻¹, and the $-SRe(=O)_3$ monomer, at 953 and 917 cm⁻¹ [94]. The gas phase dioxo $F_3Re(=O)_2$ exhibits its v_s and v_{as} vibrations at 1026 and 990 cm⁻¹. with both stretching modes higher than that observed for surface ReO₄/Al₂O₃ species. The gas phase monoxo F_5 Re=O exhibits its v_s vibration at 990 cm⁻¹, which is lower than that measured for the dehydrated surface ReO₄/Al₂O₃ species. Furthermore, the monoxo F₅Re=O does not possess the v_{as} stretching vibration observed for the surface ReO₄/Al₂O₃ species. The vibrations of the dehydrated surface ReO₄ species on Al₂O₃ (ReO₄-I: 1015, 980, 340, and 310 cm⁻¹ and ReO₄-II: 1004, 890, 340, and 310 cm⁻¹) are also remarkably similar to those of the gas phase Re₂O₇ ReO₄-containing dimer (1009, 972, 341, and 322 cm⁻¹) without the associated bridging Re–O–Re vibrational modes at 356 and 185 cm⁻¹. The similarity of the vibrations of gaseous Re₂O₇, as well as the XRe(=O)₃ oxyhalides, and the dehydrated surface ReO_x species on Al₂O₃ strongly suggests that the same coordination is present for both systems: trioxo ReO₄ with one bridging Re-O-bond. The vibrational similarity of monoxo ReO₄ and trioxo ReO₄ structures occur because both structures possess C_{3y} symmetry and the apparent degeneracy of the asymmetric vibrations of the $-O-Re(=O)_3$ functionality in gas phase dimeric Re_2O_7 . Isotopic oxygen exchange studies with Raman spectroscopy may provide further insights into the structure of the dehydrated surface $-O-Re(=O)_3$ species on Al₂O₃ because the Raman signal, unlike IR, will not be absorbed by the Al₂O₃ support below 1000 cm^{-1} .

Essentially, the same two dehydrated surface ReO_x species found to be present on Al₂O₃ are also present on ZrO₂ and TiO₂ oxide supports [42]. The coincident Raman and IR vibrations of the dehydrated ReO_x/ZrO₂ sample at low surface coverage occur at ~995 (v_s) and ~885 (v_{as}) cm⁻¹ for the first surface ReO_x species and ~1008 (v_s) and ~980 (v_{as}) cm⁻¹ for the second surface ReO_x species at the highest surface coverage (3.3 Re/nm²). The coincident Raman and IR bands for the dehydrated ReO_x/TiO₂ sample appear at ~1005 (v_s) cm⁻¹ at low surface coverage and $\sim 1011 (v_s)$ and 975 $(v_{as}) \text{ cm}^{-1}$ at the highest surface coverage (2.4 Re/nm^2) . Only very low surface coverage of ReO_x on SiO₂ was achieved (0.54 Re/nm^2) and evidence for only one dehydrated surface ReO_x species with vibrations at ~1015 (v_s) and ~985 (v_{as}) cm⁻¹ was detected on the SiO₂ support with Raman and IR, respectively. Isotopic oxygen exchange Raman studies with supported ReO_x/ZrO₂ revealed only two vibrations for Re⁼¹⁶O and Re⁼¹⁸O [76]. These results are, at first, surprising since the isotopic exchange was expected to yield four different permutations for the vibrationally coupled trioxo functionality. However, Re=O bonds that are at 90° to each other are not vibrationally coupled and would behave as independent Re=O bonds and, consequently, only give rise to splitting of the Re-O vibrations.

The molecular structure of the dehydrated surface rhenate species is shown in Figure 1.5. The surface rehenate species is always isolated and possesses three terminal Re=O bonds and one bridging Re–O support bond. The molecular structure of the dehydrated surface rhenium oxide species is consistent with the known



FIGURE 1.5 Structure of dehydrated isolated surface monoxo ReO₄ species

inorganic coordination chemistry of rhenium oxide (preference for isolated ReO₄ units with three Re=O bonds and one Re–O bond).

1.2.2.5 Molybdenum (+6) oxides

Bulk polymolybdate chains usually contain MoO₆ coordinated groups, which is unlike the polyvanadate and polychromate chains that are composed of VO₄ and CrO₄ units, respectively [60]. This reflects the preference of molybdates for higher coordination compared with vanadates and chromates in polymeric structures. However, some exceptions exist to this trend in the bulk molybdate structural chemistry. Low coordinated molybdates are present in MgMo₂O₇ (dimer of MoO₄) and in NaMo₂O₇ (chain of alternating MoO₄ and MoO₆ units). Isolated MoO₄ coordination is, however, rather common for ortho-molybdates (e.g., K₂MoO₄, Na₂MoO₄, CaMoO₄, MgMoO₄, MnMoO₄, CuMoO₄, etc.). Highly distorted, isolated MoO₄ coordination is found in Al₂(MoO₄)₃, Fe₂(MoO₄)₃, Cr₂(MoO₄)₃, and Gd₂(MoO₄)₃ [99]. Highly distorted MoO₅ units are present in Bi₂(MoO₄)₃ [99]. Polymolybdate clusters composed of 6 to 8 MoO₆ coordinated units are also known (e.g., $[NH_3P_3(NMe_2)_6]_2Mo_6O_{19}$, $(NH_4)_6Mo_7O_{24}$, and $(NH_4)_4Mo_8O_{26})$ [60,61]. Bulk alpha MoO₃ is composed of a 3D structure made up of highly distorted MoO₆ units. The large distortion present in bulk alpha-MoO₃ causes the sixth oxygen atom to be located very far from Mo and, consequently, the bulk alpha-MoO₃ structure is better described as consisting of MoO₅ units [60]. The bulk beta-MoO₃ crystalline phase is another MoO₃ 3D structure built up of less distorted MoO₆ units [53]. Several gas phase monoxo molybdenum X_4 Mo=O oxyhalides are also known and the Mo=O vibrations vary from 1008 to 1039 cm⁻¹ with increasing electronegativity of the halide (Cl < F) [61]. The gas phase dioxo $Br_2Mo(=O)_2$ gives rise to bands at 995 (v_s) and 970 (v_{as}) cm⁻¹ (electronegativity of Br < Cl < F) [61]. Thus, the structural inorganic chemistry of molybdenum oxides consists of MoO_4 , MoO_5 , and MoO_6 coordinated groups, with a preference for MoO₆ latter in polymolybdates.

The coordination of the dehydrated surface MoO_x species on different oxide supports was determined with XANES and found to be dependent on the specific oxide support and surface MoO_x coverage [40,100,101]. Above the monolayer surface MoO_x coverage, crystalline MoO_3 was also present. For supported MoO_3/SiO_2 , crystalline MoO_3 was also observed to be present significantly below monolayer surface coverage because of the low reactivity of the surface Si–OH groups. The presence of monoxo Mo=O bonds in the surface MoO_x species was revealed by the coincidence of the fundamental Raman and IR vibrations in the 980 to 1006 cm⁻¹ region and the appearance of only one band in the IR overtone region [64,85,98]. This was further confirmed by oxygen exchange studies that showed only splitting of the terminal Mo=O vibration during isotopic scrambling [76,102]. The remaining oxygen ligands in the surface MoO_x species are bonded either to the oxide support cations or to the adjacent surface MoO_x species.

For dehydrated supported MoO₃/SiO₂, both Raman and IR confirmed the absence of bridging Mo-O-Mo bonds and, thus, the presence of only isolated surface MoO_x species at low surface coverage [40,100–102]. EXAFS analysis of the dehydrated surface MoO_x species on SiO₂ is consistent with the isolated nature of the supported MoO_x/SiO₂ because of the almost complete absence of Mo–Mo neighbors in the coordination sphere [100,102]. The EXAFS analysis finds only one short Mo=O bond at 0.169 nm in the coordination sphere around Mo. The monoxo Mo=O nature of the surface MoO_x species on SiO₂ is also revealed from the identical Raman/IR vibrations of this functionality at 986 cm⁻¹ [103] and the appearance of only two IR bands during isotopic oxygen exchange (Mo=¹⁶O and Mo= 18 O) [102]. The terminal Mo=O vibrations of the dehydrated surface MoO_r species are slightly lower than the reported vibrations of the gas phase monoxo (1008 to 1039 cm⁻¹) and dioxo (995 cm⁻¹) oxyhalides. A dioxo structure would expect to exhibit a doublet in this region and only one band is observed, which is also consistent with the monoxo structure. XANES [40,100,101] and UV-Vis [104] analysis of the coordination of the surface MoO_x species on SiO₂ has been found to be neither that of pure MoO₄ nor that of pure MoO₆, and this dehydrated surface MoO_x species most probably possesses O=Mo(-O-Si)₄ coordination [40,102].

For non-SiO₂ supported MoO_x catalysts, the dehydrated surface MoO_x coordination depends on the surface molybdena coverage and the specific oxide support. At low surface molybdena coverage (5 to 15% of monolayer), primarily surface MoO₄ coordinated units are present on Al₂O₃ and TiO₂ [40,101]. The corresponding Raman spectra of these catalysts also indicate that the surface MoO₄ species are isolated on both oxide supports at low surface coverage [40,101]. This is also substantiated by the UV-Vis spectra that exhibit a high band gap value associated with isolated species [104]. At monolayer surface molybdena coverage, however, the surface MoO_x coordination is different and also dependent on the specific oxide support [40]. At monolayer surface molybdena coverage, supported MoO₃/TiO₂ was found to possess MoO₆ coordinated species and supported MoO₃/Al₂O₃ was found to possess a mixture of MoO₄ and MoO₆ coordinated groups. The additional presence of surface MoO₆ for monolayer MoO₃/Al₂O₃ was also reflected in the lower band gap energy of this catalyst [104]. The UV-Vis and Raman spectra for the dehydrated MoO₃/ZrO₂ and MoO/Al₂O₃ samples were very similar and suggest that the same surface MoO_x species exist on both supports at a given surface coverage [40,104]. The Raman spectra also exhibits the characteristics of bridging Mo–O–Mo bonds present in polymolybdates [40,101]. The coincidence of the Raman and the IR fundamental vibrations at $\sim 1000 \text{ cm}^{-1}$ for supported MoO₃/Al₂O₃ and the presence of only one band in the overtone region is consistent with monoxo Mo=O functionality [64,85,98]. This is also confirmed



FIGURE 1.6 Structures of dehydrated surface monoxo MoO_x species. (a) Isolated monoxo MoO_4/MoO_5 and (b) polymeric monoxo MoO_6

with isotopic oxygen exchange studies that reveal the presence of only two Mo=O vibrations that arise from terminal Mo=¹⁶O and Mo¹⁸O bonds [76].

The different molecular structures of the dehydrated surface molybdates are presented in Figure 1.6. At low surface molybdena coverage, the preferred coordination is isolated monoxo MoO₄, with the exception of supported MoO₃/SiO₂ that appears to possess the isolated monoxo MoO₅ structure. At high surface coverage, highly distorted and polymeric monoxo MoO₆ structures are always present. The presence of surface monoxo MoO₄ species at high surface coverage depends on the specific support (Al₂O₃ ~ ZrO₂ \gg TiO₂ ~ Nb₂O₅) [40]. For high surface coverage of supported MoO₃/SiO₂, crystalline MoO₃ is also present in addition to the surface MoO_x species. The coordination chemistry of the dehydrated surface MoO_x species parallels that of its known inorganic structural chemistry: (1) monoxo nature of the surface MoO_x species, (2) MoO₄ coordinated isolated species, (3) MoO₆ polymolybdates, (4) mixture of MoO₄/MoO₆ polymolybdates, and (6) presence of isolated MoO₅ on SiO₂.

1.2.2.6 Tungsten (+6) oxides

The structural inorganic chemistry of tungsten oxide closely mirrors that of molybdenum oxide [60,61]. Many ortho-tungstate (Li₂WO₄, Na₂WO₄, Na₂WO₄, Rb₂WO₄, and Cs₂WO₄) compounds possessing isolated WO₄ sites are known. Tungstates rarely form polymeric WO_4 compounds, and one such exception is MgW_2O_7 that consists of a pair of sharing WO_4 units. Alternating polymeric WO₄ and WO₆ sites are present in the polytungstate chains of Na₂W₂O₇ and (NH₄)₂W₂O₇. An isolated WO₅ coordinated site has been determined to be present in the Ca₃(WO₅)Cl₂ compound. Isolated WO₆ coordinated units are present in the Wolframite structure (FeWO₄, MnWO₄, CoWO₄, NiWO₄, and ZnWO₄). Polytungstate chains composed of WO₆ coordinated units are present in Li₂W₂O₇ and Ag₂W₂O₇. Tungsten oxide clusters composed of polymeric WO₆ units have been identified with varying number of tungstate units: 4-membered (Ag₈W₄O₁₆), 6-membered (NBu₄)₂W₆O₁₉, 10-membered $(NH_4BuW_{10}O_{32})$, and 12-membered (paratungstate- $(NH_4)_{10}(H_2W_{12}O_{42}.10H_2O)$) and metatungstate-(NH₄)₆(H₂W₁₂O₄₀)). Bulk WO₃ is built up a 3D structure of slightly distorted WO₆ units. Several gas phase monoxo tungsten X₄W=O oxyhalides are known (X=F, Cl, and Br) [62]. The F₄W=O gas phase complex exhibits its W=O symmetric stretch at 1055 cm^{-1} . Unfortunately, the vibrations

of the gas phase monoxo complexes Cl₄W=O and Br₄W=O have not been experimentally determined. However, it is possible to estimate their vibrational frequency by analogy with the corresponding X₄Mo=O and X₃V=O oxyhalides that are similarly influenced by the electronegativity of the halide ligands. Such a comparison suggests the monoxo W=O vibrations for Cl₄W=O and Br₄W=O oxyhalides should occur at ~1024 and ~1010 cm⁻¹, respectively. The vibrational spectra of dioxo X₂W(=O)₂ oxyhalides has not been determined, but the IR spectra for Br₂Mo(=O)₂ and the ions [Se₂Mo(=O)₂]²⁻ and [Se₂W(=O)₂]²⁻ has been reported and exhibit their v_s/v_{as} vibrations at 995/970, 864/834, and 888/845 cm⁻¹, respectively [62]. Note that the selenium-containing dioxo ions exhibit similar vibrations, but the W-containing ion vibrates ~10 to 24 cm⁻¹ higher than the corresponding Mocontaining ion. This suggests that gas phase Br₂W(=O)₂ oxyhalide would vibrate at ~1020/980 cm⁻¹ by analogy with Br₂Mo(=O)₂. This value can increase further as the electronegativity of the halides increases (Br < Cl < F), which may shift these bands to ~1030/990 to 1050/1010 cm⁻¹.

The coordination of dehydrated surface WO_x species on different oxide supports was examined with XANES and found to vary with the surface tungsten oxide coverage and oxide support [48-50]. Above the monolayer coverage for the non-SiO₂ supports, crystalline WO₃ particles are present on top of the surface tungsten oxide monolayer [50,83,105,106]. In the case of supported WO₃/SiO₂, crystalline WO₃, and surface WO_x species are simultaneously present below monolayer surface coverage due to the low reactivity of the Si-OH groups [106,107]. For the supported WO_x systems that were extensively examined with Raman and IR, it was concluded that the surface WO_x species contain only one terminal W=O bond [85,98]. The fundamental vibrations of the terminal W=O bond was found to be coincident in the Raman and IR spectra, and only one band was observed in the IR overtone region. Isotopic oxygen exchange studies further confirmed the monxo W=O nature of the surface WO_x structures since only two bands due to $W=^{16}O$ and $W=^{18}O$ vibrations were detected [108]. The vibrations of the terminal W=O bond of the dehydrated surface WO_x species occur at 985 to 1025 cm⁻¹ and are in the vibrational range expected for gas phase oxyhalide monoxo tungstanyls (1022 to 1055 cm⁻¹). Thus, the surface WO_x species contain one terminal W=O bond and bridging W-O support and W-O-W bonds for polytungstates.

For dehydrated supported WO₃/SiO₂, the Raman spectra exhibits a single band at ~983 cm⁻¹ that has been assigned to the vibration of the terminal W=O bond [108]. The position of this vibration is below that of the gas phase monoxo and dioxo tungsten oxyhalides (1010 to 1055 cm⁻¹). Unfortunately, no corresponding IR and isotopic oxygen exchange studies have yet been reported for this system to allow discrimination between monoxo and dioxo functionalities. In addition, no XANES and UV-Vis characterization studies about the coordination of the surface WO_x species on SiO₂ have been reported till date. Although, much of the critical structural spectroscopic data about the surface WO_x species on SiO₂ are currently not available, comparison with the corresponding surface MOO_x/SiO₂ system tentatively suggests that the surface WO_x on SiO₂ most likely possesses the isolated monoxo $O=W(-O)_4$ structure. The actual details of the surface WO_x structure on SiO₂ will be determined once the additional characterization information becomes available.

For dehydrated non-SiO₂ supported WO_x , there currently exists sufficient Raman and IR data to conclude that these structures possess monoxo W=O surface WO_x species. For supported WO₃/Al₂O₃, the coincidence of the Raman and IR bands at $\sim 1010 \text{ cm}^{-1}$ for low surface coverage and $\sim 1020 \text{ cm}^{-1}$ for high surface coverage and the presence of only one band in the IR overtone region are consistent with the presence of a monoxo W=O functionality [85,98]. This was further substantiated with isotopic oxygen exchange studies that only revealed the presence of only $W=^{16}O$ and $W=^{18}O$ vibrations [108]. The coordination of the surface WO_x species on Al₂O₃ was found to be WO_4 at low surface coverage and WO₆ at monolayer coverage [48]. Raman spectroscopy also revealed the presence of bridging W–O–W bonds with $v_s = 590 \text{ cm}^{-1}$ and the corresponding 215 cm⁻¹ bending mode at high surface coverage, but not at low surface coverage [83]. The above information suggests that at low surface coverage the dehydrated surface WO_x species are isolated and at high surface coverage they are present as polytungstates. The analogous XANES and IR results were found for supported WO₃/TiO₂, with the only difference being the proposed surface WO₅ structure at high surface coverage [49,109]. For supported WO_3/ZrO_2 , the surface WO_x species have been proposed to be present as isolated monoxo surface WO₆ species at all coverage from combined Raman, UV-Vis, and XANES/EXAFS studies [50]. Isotopic oxygen exchange Raman studies are consistent with the monoxo surface WO₆ structure on ZrO₂ since isotopic exchange only resulted in splitting of the W=O bond and the isotopic shift was consistent with that predicted for a monoxo structure [76]. The proposed isolated nature of the surface WO_6 species on ZrO_2 needs to be further confirmed since the absence of polymeric WO₆ species at monolayer surface coverage is a rather surprising result for surface metal oxides on ZrO₂.

The dehydrated molecular structures of surface WO_x are presented in Figure 1.7. Analogous to the dehydrated surface MO_x species, dehydrated isolated surface WO_4/WO_5 and dehydrated polytungstate surface WO_6 species are also found. The isolated monoxo WO_4 and WO_5 species are primarily observed at low surface coverage and the polytungstate monoxo WO_6 species are found to be present at high surface coverage. These dehydrated surface WO_x structures are consistent with the known inorganic chemistry of tungsten oxide compounds.



FIGURE 1.7 Structures of dehydrated surface monoxo WO_x species. (a) Isolated surface monoxo (WO₄ and WO₅) and (b) polymeric surface monoxo surface

1.2.2.7 Niobium (+5) oxides

Bulk niobium (+5) oxides primarily possess distorted NbO₆ coordination with different extents of distortion [60,110]. The NbO7 and NbO8 coordination are also known (e.g., Nb₂O₅·nH₂O is composed of NbO₆, NbO₇, and NbO₈ units). Isolated NbO₄ coordination is not common and only found in several rare earth niobates: LaNbO₄, SmNbO₄, YbNbO₄, and YNbO₄. Consequently, unlike the isolated MO₄ sites present in bulk AlVO₄, Al₂(MoO₄)₃, and Al₂(WO₄)₃ discussed earlier, the bulk AlNbO₄ structure contains highly distorted polymeric NbO₆. The Nb₆O₁₉ cluster is present in K₈Nb₆O₁₉, as well as in other Nb salts, and is composed of distorted NbO₆ groups. The decaniobate Nb₁₀O₂₈ cluster, analogous to the decavanadate cluster, is built up of distorted NbO₆ groups and has been isolated in the $[N(CH_3)_4]_6Nb_{10}O_{28}$ salt. Layered niobia salts, $KCa_2Na_{n-3}Nb_nO_{3n+1}$ with n = 3 to 5 layers, are composed of distorted monoxo NbO₆ groups [111–113]. The various bulk Nb₂O₅ crystalline phases are built up of 3D structures made up of distorted NbO₆ units with minor NbO₇ and NbO₈ sites (TT and T phases) and minor NbO₄ sites are also found in the holes of H-Nb₂O₅ (1 NbO₄ per 27 NbO₆). The Nb=O vibrations of monoxo Cl₃Nb=O and dioxo $S_2Nb(=O)_2^{3-}$ oxyhalides occur at 997 and 897/872 cm⁻¹, respectively [61]. Thus, the inorganic structural chemistry of niobia compounds is mostly made up of distorted NbO₆ units, with some structures also containing NbO7 and NbO8 groups, and the isolated NbO4 structure is rare.

The XANES/EXFAS data are only available for the dehydrated supported Nb₂O₅/Al₂O₃ and Nb₂O₅/SiO₂ systems [67]. The XANES/EXAFS analyses suggest that surface NbO₄ species are present at low surface coverage on both oxide supports. At high surface coverage on Al₂O₃, dehydrated surface NbO₆ species become the dominant surface NbO_x species [114]. At high surface coverage on SiO₂, crystalline Nb₂O₅ coexists with the surface NbO₄ species because of the low reactivity of the surface Si–OH bonds [114,115]. Above the monolayer surface coverage, crystalline Nb₂O₅ particles form on all oxide supports after calcination. The highest Raman vibration observed for the surface NbO₄ species is detected at \sim 980 to 990 cm⁻¹ and occurs at almost the same vibration for the gaseous monoxo Cl₃Nb=O oxyhalide, 997 cm⁻¹, which is significantly greater than the dioxo vibrations observed at 897 and 872 cm^{-1} [62,115]. The corresponding IR bands are coincident with the Raman vibrations and only one Nb=O vibration is present in the overtone region [116]. This collective spectroscopic information points to the presence of dehydrated isolated, monoxo surface O=Nb(-O)₃ species at low surface coverage. At high surface NbO_x/Al₂O₃ coverage, the XANES/EXAFS analyses suggest NbO₆ coordination and additional strong bands are present in the Raman spectra at ~950, 880, and 645 cm⁻¹associated with bridging Nb-O-Nb bonds. The Raman and IR bands at \sim 985 cm⁻¹ are essentially coincident, and only one band is observed in the overtone region. This collective spectroscopic information suggests a dehydrated, distorted monoxo NbO₆ surface species at high surface coverage. Very similar Raman and IR vibrations are also present for the dehydrated supported Nb₂O₅/ZrO₂ and Nb₂O₅/TiO₂ systems. Isotopic oxygen



FIGURE 1.8 Structures of dehydrated surface monoxo NbO_x species. (a) Isolated surface monoxo niobate (NbO₄) and (b) polymeric surface monoxo niobate (NbO₆)

exchange Raman studies of monolayer supported Nb₂O₅/ZrO₂ reveal only two bands at ~980 and ~930 cm⁻¹ due to Nb=¹⁶O and Nb=¹⁸O vibrations, and further support the presence of monoxo surface NbO₆ species [76]. Thus, under dehydrated conditions, isolated monoxo surface NbO₄ and polyniobate monoxo NbO₆ species are present on the oxide supports at low and high surface coverage, respectively. The proposed structures of the dehydrated surface NbO_x species are depicted in Figure 1.8.

The dehydrated surface NbO_x coordination chemistry is consistent with the known Nb oxide inorganic structural chemistry. Whereas NbO_4 coordination is rare in Nb inorganic structural chemistry, the surface NbO_4 structure appears to be prevalent at low surface coverage on oxide supports under dehydrated conditions.

1.2.2.8 Tantalum (+5) oxides

The bulk structural inorganic chemistry of tantalum oxide essentially mirrors that of niobium oxide [60,61,68]. Isolated TaO₄ sites are rare (e.g., YbTaO₄) and TaO₆ coordinated compounds are most common. Like niobia, tantala can also exhibit TaO₇ and TaO₈ coordination. The salt $K_8(Ta_6O_{19}) \cdot 16H_2O$ contains the $Ta_6O_{19}^{8-}$ cluster, similar to the $Nb_6O_{19}^{8-}$ cluster described in Section 1.2.2.7, made up of distorted TaO₆ groups. Bulk Ta₂O₅ exhibits a phase transition at 1360°C and the stable phases below and above this temperature are referred to as L-Ta₂O₅ and H-Ta₂O₅, respectively. Poorly crystalline Ta₂O₅ is present below \sim 800°C and is present as Ta₂O₅·nH₂O (tantalum oxhydrate). Both the L-Ta₂O₅ and H-Ta₂O₅ crystalline phases consist of a three-dimensional network of distorted TaO₆ and TaO₇ units. The vibrational spectra of gaseous Ta oxyhalide complexes have not been reported in the literature [61,62]. It is possible, however, to estimate the vibrational band position of a monoxo Cl₃Ta=O bond by comparing with the corresponding Cl₃Nb=O monoxo complex and correcting for the heavier mass of Ta. Such an estimation gives a value of \sim 950 cm⁻¹ for the Ta=O vibration [68]. An analogous estimation of the vibrations for dioxo O=Ta=O suggests two vibrations in the 800 to 860 cm⁻¹ region. Thus, the structural chemistry of tantala compounds rarely consists of TaO₄ coordination and is mostly made up of distorted TaO₆ and TaO_7 (TaO₈) units.

The coordination of the dehydrated surface TaO_x species on several different oxide supports was determined with XANES [68]. Highly distorted TaO_6 species were primarily found to be present on Al₂O₃, ZrO₂, and TiO₂ supports at high surface coverage. UV-Vis characterization of the dehydrated supported Ta_2O_5/Al_2O_3



FIGURE 1.9 Structures of dehydrated surface monoxo TaO_x species. (a) Isolated surface monoxo tantalate (TaO_4) and (b) polymerized surface monoxo tantalate (TaO_6)

and Ta₂O₅/ZrO₂ catalysts also resulted in similar assignments [117]. The polymeric nature of these dehydrated surface TaO₆ species is reflected in the presence of bridging Ta–O–Ta vibrations at ~740 (v_{as}) and ~610 (v_s) cm⁻¹ in the corresponding Raman spectra. For dehydrated Ta₂O₅/SiO₂, however, XANES and UV-Vis analyses revealed only the presence of TaO₄ units on the SiO₂ surface and Raman does not exhibit bands typically associated with bridging Ta–O–Ta bonds [68,117]. The Raman bands for the Ta=O functionality appeared at ~940 cm⁻¹, which is consistent with the monoxo functionality of the dehydrated surface tantala species. Thus, for high surface coverage the dehydrated surface tantala species on Al₂O₃, ZrO₂, and TiO₂ primarily consist of polymeric TaO₆ units and as isolated TaO₄ units on SiO₂. The dehydrated surface TaO₄ coordination is probably also present at low surface coverage on the oxide supports, as found for the dehydrated surface NbO_x species, but such data has not been reported in the literature till date. The proposed structures for the dehydrated surface TaO_x species are shown in Figure 1.9.

The molecular structures of the dehydrated surface TaO_x species reflect the inorganic chemistry of tantalum oxide and mirror that of the analogous surface niobium oxide species. Isolated surface TaO_4 is present on SiO_2 and probably also at low surface coverage on all the oxide supports. Polytantalate TaO_6 species are the dominant species at high surface tantalum oxide surface coverage.

1.2.3 Surface Metal Oxide Species in Reactive Environments

In situ characterization studies of the surface metal oxide species under reactive environments for supported metal oxide catalysts have only appeared in the literature over the past decade [63,66,75,83,93,114]. For surface metal oxide species that usually do not undergo redox processes (acidic WO₃, Nb₂O₅, and Ta₂O₅), the surface metal oxide molecular structures under reactive conditions are identical to those present for the dehydrated conditions discussed earlier. For surface metal oxide species that can undergo redox processes (V₂O₅, CrO₃, MoO₃, and Re₂O₇), both, fully oxidized and partially reduced surface metal oxide species can be present. The fraction of reduced surface species is dependent on the reduction potential of the specific surface metal oxide (Re > V > Cr > Mo), and the specific reactive environment (partial pressures of reducing reactant/O₂ and the specific reducing reactant (e.g., propylene > *n*-butane > propane > ethane > methane) and the specific reactive environment (temperature and ratio of reducing agent/O₂)). At present, the molecular structures of the dehydrated reduced surface metal oxide species present for supported metal oxide catalysts under reactive environments are not well-known and, hopefully, will receive more attention in the coming years. Fortunately, the fully oxidized surface metal oxide species are the predominant species found to be present under typical reaction conditions employed for redox supported metal oxide catalysts.

1.3 Molecular Sieves and Zeolites

Molecular sieves and zeolites are highly porous, crystalline metal oxides made up of three-dimensional channel structures where every atom is on the surface and exposed to the reactive environment (100% dispersed) [118]. Zeolites consist of AlO₄ and SiO₄ units with or without other cations and the term molecular sieves is reserved for SiO₄-based systems that are free of Al and typically doped with other cations. Zeolites find wide application in the petroleum industry as catalytic acidic materials for fluid catalytic cracking (FCC) of crude oil. Molecular sieves have been shown to exhibit surface redox properties and find application as catalysts for liquid phase epoxidation of olefins with H2O2. Recent characterization studies comparing cation-containing molecular sieves (e.g., Ti, V, and Nb) have revealed that essentially the same dehydrated surface metal oxide species are present in the doped molecular sieves and the amorphous SiO₂ supported metal oxide analogs. For example, isolated VO₄ sites were found to be present for both dehydrated V-silicalite and supported V2O5/SiO2 catalytic systems [119]. For dehydrated Ti-silicalite and supported TiO₂/SiO₂ at low surface coverage, isolated TiO_4 units have been shown to be present for both systems [120]. Similarly, both dehydrated Nb-MCM-41 and supported Nb₂O₅/SiO₂ catalytic materials contain isolated NbO₄ sites [114]. The same situation also occurs for surface acidic sites generated by zeolites such as Al-ZSM5 and supported Al₂O₃/SiO₂ [121]. Thus, the above molecular structural descriptions for the surface metal oxide species present in SiO₂ supported metal oxide catalysts also apply to isolated metal oxide active sites present in molecular sieve catalytic materials.

1.4 Bulk Mixed Metal Oxides

Bulk mixed metal oxide catalytic materials consist of multiple metal oxide components. Such mixed metal oxide catalysts find wide application as selective oxidation catalysts for the synthesis of chemical intermediates. For example, bulk iron-molybdate catalysts are employed in the selective oxidation of CH₃OH to H₂CO [122], bulk bismuth-molybdates are the catalysts of choice for selective oxidation of CH₂=CHCH₃ to acrolein (CH₂=CHCHO) and its further oxidation to acrylic acid (CH₂=CHCOOH) [123], selective ammoxidation of CH₂=CHCH₃ to acrylonitrile (CH₂=CHCN) [123], and selective oxidation of linear CH₃CH₂CH₂CH₃ to cyclic maleic anhydride consisting of a five-membered ring (four carbons and one O atom) [124]. The characterization of the surface metal oxide sites present for the bulk mixed metal oxide catalytic materials has been one of the most challenging undertakings because the same elements are present both on the surface and in the bulk of these materials. Consequently, very few characterization methods exist that are able to selectively structurally probe the outermost surface metal oxide sites present in bulk mixed metal oxides. The typical surface science techniques based on electron spectroscopic methods probe the surface region 0.5 to 3 nm and are not limited to the ousstermost surface layer (<0.5 nm). The usual catalyst characterization methods of Raman, IR, UV-Vis, NMR, and XANES/EXAFS are all bulk characterization methods and their spectra are usually dominated by signals from the bulk rather than the outermost surface layer. In the past few years, however, characterization studies employing low energy ion scattering spectroscopy (LEISS) [125,126] chemical probe molecules [127,128], synchrotron-based surface XPS [129] are revealing that the surfaces of bulk mixed metal oxides possess compositions that are different than those found in the bulk of these catalytic materials. Surprisingly, the surfaces of many molybdate and vanadate mixed metal oxides have revealed the exclusive presence of surface molybdenum oxide and vanadium oxide monolayers. At present, the molecular structures of these outermost surface metal oxide monolayers have not been determined. It is possible, however, that these outermost surface metal oxide monolayers of bulk mixed metal oxides also possess the same molecular structures found for the surface metal oxide species present in supported metal oxide catalysts. Hopefully, these issues can be resolved in the coming years.

1.5 Conclusions

Significant advances in determining the molecular structures of the surface metal oxide species of metal oxide materials, the catalytic active sites, have been achieved in recent years. These advances have been made possible by the application of modern molecular spectroscopic characterization techniques (Raman, IR, UV-Vis, XANES, EXAFS, and NMR). A very important aspect of these molecular spectroscopic techniques is their ability to collect spectroscopic data under different environmental conditions since the molecular structures of the surface metal oxide species are dynamic and environmentally dependent. The surface metal oxide species are presented as hydrated metal oxide species under ambient conditions that are essentially the same as the well-known aqueous metal oxide species. Upon dehydration, these metal oxide species coordinate with the oxide support substrates to form surface metal oxide species, for the group 5 to 7 metal oxides, that terminate with monoxo M=O terminal bonds. The dehydrated surface metal oxides can be present as isolated species with only bridging M-O Support bonds as well as polymeric species with additional bridging M-O-M bonds. Above the monolayer surface coverage, crystalline metal oxides form on top of the surface metal oxide monolayer. The surface molecular structures found to be present under reactive environments are the dehydrated surface metal oxide species. Depending on the reducing/oxidizing environmental conditions, reduced surface metal oxide species may also be present. At present, very little structural information is available about these reduced surface metal oxide species. Essentially the same surface metal oxide structures are found to be present for corresponding supported metal oxide, molecular sieve, and zeolite materials. The surface molecular structures present for bulk mixed metal oxides are not known at present. In spite of this impressive recent progress, the molecular structures of many oxidized and reduced surface metal oxide species have not been completely determined or are not even known at present. Consequently, many more fundamental structural studies are still required to obtain complete determination of the molecular structures of surface metal oxide species under different environmentally conditions.

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2 Nanostructured Supported Metal Oxides

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2.1 INTRODUCTION

Supported catalysts comprise a very general solid catalyst design in which the active phase (the supported layer) is located on the surface of an underlying solid (the support). The motivation for supported catalysts is that the dispersion and stabilization of the supported layer on a high surface area support leads to a highly active and robust composite catalyst. Metals, metal oxides, metal

sulfides, organometallic complexes, and enzymes can be supported on inorganic supports such as metal oxides, zeolites, and clays. This subject matter has been well documented by a number of books [1–4] and more recently by *Preparation of Solid Catalysts* [5], a monograph based on the comprehensive *Handbook of Heterogeneous Catalysis* volumes edited by Ertl et al. [6].

Supported catalysts in which a metal oxide is supported on a different metal oxide find tremendous use in commercial chemical production, petroleum refining, and environmental remediation [7]. Table 2.1 lists a number of important industrial reactions that are catalyzed by supported metal oxides. The active phase consists of single metal oxides, metal oxide mixtures, or complex metal oxides. Some supported metal catalysts can, technically, be considered supported metal oxide catalysts if the metal is partially oxidized under reaction conditions, such as alumina-supported silver epoxidation catalysts and palladium-on-stabilized alumina combustion catalysts. Clearly, supported metal oxide compositions are diverse, especially considering that the range of relative amounts of the active phase to the support is large, and that additional metal oxides and modifiers can be introduced.

It can be argued that some mixed metal oxides can also be technically considered as supported metal oxide catalysts because the surface is discernibly different from the underlying mixed metal oxide in terms of composition and molecular structure. For example, the vanadium phosphorus oxide (VPO) catalyst is used in the commercial production of maleic anhydride from butane [12]. The most active crystal phase is the vanadium pyrophosphate (VO)₂P₂O₇, and the surface structure proposed to be the active phase is a nanometer-thick amorphous VPO layer enriched in phosphorus [12,15]. As another example, Wachs and coworkers [16]

TABLE 2.1Commercial Processes [3,4]

Supported metal oxide compositions	Catalytic reaction
$V_2O_5/(Kieselguhr \text{ or } SiO_2)$	Oxidation of SO ₂ for sulfuric acid production
(V ₂ O ₅ +WO ₃)/TiO ₂	Selective catalytic reduction of NO_x using ammonia [8]
$(V_2O_5+MoO_3)/Al_2O_3$	Oxidation of benzene to maleic anhydride
V ₂ O ₅ /TiO ₂	Oxidation of o-xylene to phthalic anhydride [9]
Cr_2O_3/Al_2O_3	Dehydrogenation of light alkanes to alkenes [10]
CrO_x/SiO_2	Ethylene polymerization [11]
$(K_2O+Cr_2O_3)/Fe_2O_3$	Dehydrogenation of ethylbenzene to styrene
Bi9PMo12O52/SiO2	Ammoxidation of propene to acrylonitrile [12]
Re ₂ O ₇ /Al ₂ O ₃	Olefin metathesis [13]
TiO ₂ /SiO ₂	Dehydration of phenylethanol to styrene
TiO ₂ /SiO ₂	Epoxidation of propylene with ethylbenzene hydroperoxide [14]
AgO_x/γ - Al_2O_3	Oxidation of ethylene to ethylene oxide
$(PtO_x + PdO_x)/(La_2O_3 + Al_2O_3)$	Catalytic combustion of volatile organic compounds [12]

provided methanol chemisorption data which indicate that mixed metal molybdates and supported molybdenum oxides have similar surface structures.

In this chapter, the common methods of supported metal oxide catalyst preparation are presented. The molecular and nanoscale structure (i.e., textural properties) of supported metal oxides, specifically tungstated zirconia, are also discussed. Finally, several new synthesis techniques are presented, through which simultaneous control of the molecular and nanoscale structures may be possible.

2.2 METHODS OF PREPARATION

The basic principle behind supported metal oxide catalyst preparation involves deposition followed by activation. According to The International Union of Pure and Applied Chemistry (IUPAC) recommendations, deposition is defined as "the application of the catalytic component on to [sic] a separately produced support," and activation as "the transformation of the precursor to the active phase," usually entailing the calcination of the composite material [17]. There are several well-studied deposition steps, with impregnation being the most common method for preparing industrial supported metal oxides.

2.2.1 Impregnation

Contacting the support material with a solution that contains the supported metal oxide precursor is known as impregnation. The incipient wetness method is impregnation in which the support is contacted with a volume of precursor solution slightly in excess of the total pore volume of the support, and then the slightly wet powder is allowed to dry. This particular method allows a wide range of loadings to be possible, regardless of the surface interactions between the precursor and the support that would limit the overall loading (e.g., adsorption and ion exchange).

If the support material is initially in the dry state, then the deposition process is called capillary, or dry, impregnation. The speed of pore filling is fast and the process is simple, but there are potential problems of heat release and internal pore collapse due to capillary pressure by entrapped air [18]. If the support is already in contact with the solvent (without the precursor), then the subsequent contact with the precursor solution is known as diffusional, or wet, impregnation.

2.2.2 Ion exchange

Impregnation through ion exchange (or equilibrium adsorption) involves immersing of the support material in an aqueous solution of the supported metal oxide precursor, and recovering the solid from the solution after a period of time. The charged salt precursor electrostatically binds to the oppositely charged surface of the support (typically a metal oxide). The surface charge arises from the difference in the pH of the aqueous solution and the point-of-zero charge (PZC) of the metal oxide support. If the pH > PZC, then the terminating hydroxyl groups at the surface deprotonate. The net surface charge is negative, and the surface can adsorb cationic species. Conversely, if the pH > PZC, the hydroxyl groups protonate and the surface can adsorb anionic species. It is difficult to differentiate between electrostatic attraction and strict ion exchange of the precursor and the surfacebound counterion. Other chemical interactions can also take place, such as metal coordination.

2.2.3 Grafting

Grafting involves covalent bond formation between the metal precursor and the hydroxyl group(s) on the support. This is more readily controlled as a preparation method in which the support is contacted with the precursor solubilized in a nonaqueous solvent. Common precursors are metal alkoxides, metal chlorides, and organometallic complexes. Both ion exchange and grafting methods lead to coverage by the precursor up to a monolayer, but the latter allows a greater control of dispersion and molecular structure of the supported metal species. Grafting can also be carried out using precursors vaporized in the gas-phase, and this method of catalyst preparation is called chemical vapor deposition (CVD).

2.2.4 Deposition-Precipitation

Like incipient wetness impregnation, this method provides supported metal oxides with high loadings. The support material is suspended in a precursor solution, and then precipitation of the supported metal oxide is induced such that the metal oxide nanoparticles (NPs) are nucleated and grown on internal and external surfaces of the support.

2.2.5 Co-Precipitation

Supported metal oxides can be prepared through co-precipitation, in which metal precursors to both the support and the supported metal oxide are induced to form the support material and the supported layer simultaneously. The support and the supported metal oxide are more spatially distributed than materials derived from the various deposition methods, but a fraction of the supported metal oxide may be located below the surface, leading to overall lower metal oxide dispersion.

2.2.6 Other Methods

Other methods for preparing supported metal oxides have been reported. An interesting approach is the use of bulk MoO₃ in the preparation of MoO_x/Al₂O₃. In the solid–solid wetting or thermal spreading approach, MoO₃ and Al₂O₃ powders are mechanically ground together and heated at elevated temperatures (\sim 500°C) for 24 h to yield MoO_x/Al₂O₃ [19]. The ability of MoO₃ to spread across the Al₂O₃ surface as MoO_x surface species is attributed to the relatively low melting point and Tammann temperatures of MoO₃ (795 and 261°C, respectively), the affinity of the acidic MoO₃ surface for the basic Al₂O₃ surface, and the reduction in surface energy of the bulk solids to form a supported metal oxide structure. Instead of calcination, refluxing MoO₃ and Al₂O₃ powders in water for several hours can also yield the supported material [20]. In this slurry impregnation method, MoO₃ partially decomposes in water and the solubilized Mo species deposit on the support. The resulting material is structurally similar to conventionally prepared MoO_x/Al₂O₃.

2.3 CATALYST MOLECULAR STRUCTURE

After the deposition (or co-precipitation) step, the resultant material is calcined to decompose the metal precursor to form the supported metal oxide layer. Several different surface metal oxide structures can emerge (Figure 2.1), which depends on the preparation method, the metal oxide loading, the specific surface area of the underlying supporting substrate, and the solid-solid chemical interactions between the support and the supported layer. At low loadings, the metal oxide precursor can be dispersed as isolated metal (monomeric) species. Increased loadings leads to the adjoining mono oxo species forming oligomeric or polymeric species via metal-oxygen-metal linkages, and eventually, to surface-bound (nano)crystalline metal oxide domains. In addition to these structures, the metal oxide precursor can form a solid solution with the support (e.g., $Al_2(WO_4)_3$ resulting from the preparation of WO_x/Al_2O_3 [21] and MgWO₄ resulting from the preparation of WO_x/MgO [22]) or a surface species of a mixed metal oxide composition (e.g., supported aluminotungstate clusters on WO_x/Al₂O₃ [23]). Identification of surface structures and elucidation of structure-property relationships for many supported metal oxide compositions have been enabled by in situ/operando Raman and other surface-sensitive spectroscopic techniques in recent years [24-29].

An important parameter in determining the structure of the supported layer is the surface density of the metal center (ρ_{surf}). This is experimentally determined from the measured weight loading of the supported metal oxide and the overall BET surface area of the catalyst. Quantitatively,



FIGURE 2.1 Representations of possible molecular structures of supported metal oxide

where the units of ρ_{surf} and surface area are (metal atom)/nm² and m²/(g of material), respectively, and the molecular weight is that of the supported metal oxide. The surface density represents an average value and not the actual metal distribution. There is the implicit assumption that the supported layer is localized at the support surface, which may not hold for all supported metal oxides. Thus, the actual surface density values of co-precipitated supported metal oxides may be overestimated by ρ_{surf} calculations if a portion of the supported phase is entrapped within the support structure. Nevertheless, it is a useful metric for describing supported metal oxides.

2.4 Case Study: TUNGSTATED ZIRCONIUM OXIDE

Tungstated zirconia is discussed as an illustration of some of the important concepts of supported metal oxides. This supported catalyst composition has exceptional low-temperature activity for acid-catalyzed reactions, as first reported by Hino and Arata [30] for light alkane isomerization over 15 years ago. There has been a continued interest in these WO_x/ZrO₂, materials as a robust alternative to sulfated zirconia and other acid catalysts in industrial acid catalytic processes [31–33], and progress has been made in understanding the nature of acidity and the relationship between the surface structure and catalytic behavior. WO_x/ZrO₂ can be doped with iron, platinum, sulfate, and other species for improved catalytic properties [34–39]. The short-hand notations "WO₃/ZrO₂" and "WO_x/ZrO₂" are commonly used, with the latter term more appropriate as it indicates the variable surface structures of the supported tungstate species (i.e., monomeric, polymeric, and crystalline).

Different routes have been studied in the synthesis of WO_x/ZrO_2 , since Hino and Arata's original report, with many variations of the incipient wetness impregnation theme (Table 2.2). The sol–gel approach is not well studied, and will be discussed in Section 2.5.3. For impregnation, crystalline ZrO_2 (tetragonal or monoclinic phases, or a mixture of both) and amorphous ZrO_2 (variously written as $Zr(OH)_4$, $ZrO(OH)_2$, or $ZrO_x(OH)_{4-2x}$) have been used. Prepared through a proprietary process, uncalcined WO_x/ZrO_2 is commercially available from MEL Chemicals (Magnesium Elektron Inc., USA) [40,41].

Common observations about WO_x/ZrO_2 can be drawn, which is independent of the preparation method:

- WO_x species suppress the sintering of the ZrO₂ support and the crystallization of amorphous ZrO₂.
- Higher calcination temperatures lead to lower surface areas and therefore higher surface densities, for a given weight loading.
- High weight loadings and high calcination temperatures lead to the formation of WO₃ crystals.
- WO_x/ZrO₂ with the same surface density can have different WO₃ weight loadings.

TABLE 2.2 Conventional Preparation Methods for WO_x/ZrO_2

Authors	Method	Precursor source and activation procedure
Hino and Arata,	Incipient wetness	ZrO ₂ source: Zr(OH) ₄ precipitated from zirconyl
1988 [30]	impregnation	chloride using NH ₄ OH
		WO_x source: ammonium metatungstate solution
		Calcined in air, 600 to 1000°C
Santiesteban	Incipient wetness	ZrO ₂ source: Zr(OH) ₄ precipitated from zirconyl
et al., 1997 [42]	impregnation	chloride using NH ₄ OH; dried at 95°C; refluxed in NH ₄ OH solution overnight
		WO_x source: ammonium tungstate solution
		Calcination at 825°C for 3 h in air
	Co-precipitation	ZrO ₂ source: Zirconyl chloride solution added to NH ₄ OH/ammonium tungstate solution
		WO_x source: ammonium tungstate solution
		Precipitate was placed in a steambox at 100°C
		for 16 h before calcination at 825°C for 3 h in air
Vaudagna et al.,	Incipient wetness	ZrO ₂ source: Zr(OH) ₄ precipitated from zirconyl
1997 [43]	impregnation	chloride using NH ₄ OH; dried at 110°C
		WO_x source: ammonium tungstate solution
		Calcination at 800°C for 3 h in air
Yori et al.,	Incipient wetness impregnation; ion exchange	ZrO ₂ source: Zr(OH) ₄ precipitated from zirconyl
1997 [44]		chloride using NH ₄ OH; dried at 110°C
		WO_x source: ammonium tungstate solution
		Calcination at 800°C for 3 h in air
Boyse and Ko, 1997 [45]	Incipient wetness impregnation	ZrO ₂ source: ZrO ₂ aerogel derived from zirconium <i>n</i> -propoxide through CO ₂ supercritical drving at 70°C
		WO_r source: ammonium tungstate solution
		Calcination at 700 to 1000°C for 2 h in air
	Co-gelation	ZrO ₂ source: Zirconium <i>n</i> -propoxide gelled with ammonium tungstate solution
		WO_x source: ammonium tungstate solution
		Gel was supercritical dried in CO_2 at 70°C, dried at 110 and 250°C, and calcined at 700 to 1000°C in air
Scheithauer	Modified incinient	Z_{rO_2} source: $Z_r(OH)_4$ supplied by MEL Chemicals
et al., 1998 [46]	wetness	WO _x source: ammonium tungstate solution
	impregnation	Suspension was refluxed at 110°C for 16 h, dried at 110°C for 12 h, calcined between 500 and 1000°C for 3 h
Barton et al.,	Incipient wetness	ZrO ₂ source: Zr(OH) ₄ precipitated from zirconyl
1999 [47]	impregnation	chioride using NH_4OH ; dried at 150°C
		w O_x source: ammonium tungstate solution
		Samples calcined between 500 and 1010°C for 3 h in air

Authors	Method	Precursor source and activation procedure
Naito et al., 1999 [48]	Incipient wetness impregnation	ZrO ₂ source: Zr(OH) ₄ precipitated from zirconium oxynitrate using NH ₄ OH WO _x source: ammonium tungstate solution
		Calcination at 650°C for 4 h in air
Valigi et al., 2002 [49]	Incipient wetness impregnation; ion exchange	ZrO ₂ source: Zr(OH) ₄ precipitated from zirconyl chloride using NH ₃ gas; dried at 110° C WO _x source: ammonium tungstate solution Calcination at 800°C for 5 h in air

TABLE 2.2 Continued.

2.4.1 Surface Coverage

Monolayer or saturation coverage can be defined as the surface density above which nanocrystals of the supported phase can be detected through Raman spectroscopy. Wachs and coworkers reported that the monolayer coverage was $\sim 4 \text{ W/nm}^2$ for WO_x/ZrO₂ (prepared through incipient wetness impregnation) [22]. Other supports such as TiO₂, Al₂O₃, Nb₂O₅, and Ta₂O₅ were reported to have similar values for W monolayer coverages [22,25,50]. The term "monolayer catalyst" is occasionally used to refer to a supported metal oxide catalyst with monolayer coverage [9,51].

Different surface structure models lead to a range of theoretical monolayer coverages. Zhao et al. calculated that a close-packing of WO₃ units in which the oxygens form a complete monolayer on a ZrO₂ (or any) surface would have a theoretical surface density of 0.19 g WO₃ per 100 m², or 4.93 W/nm² [52,53]. Scheithauer et al. [46] considered 6.5 W/nm² to be the theoretical monolayer, based on the surface area of a WO₃ unit derived from the bulk density of crystalline WO₃. Iglesia and coworkers [47] indicated that a range of 7 W/nm² [54,55] to 7.8 W/nm² can be calculated for the theoretical monolayer coverage for polytungstates from "the density of WO_x species in a two-dimensional plane of corner-shared WO₆ octahedra with W–O bond distances corresponding to those in low-index planes of monoclinic WO₃ crystallites" [47].

From a molecular standpoint, WO_x surface species can be thought to titrate the ZrO₂ surface hydroxyl groups. Scheithauer et al. [56] performed *in situ* fourier transform infrared (FTIR) spectroscopy on a series of WO_x/ZrO_2 prepared through a modified incipient wetness impregnation method. They found that surface Zr–OH groups (corresponding to an infrared (IR) peak between 3765 and 3782 cm⁻¹) of the ZrO₂ support decreased in population with increasing WO_x loading and disappeared at 4.0 W/nm². They also detected IR peaks in the O–H stretching region at lower wavelengths (between 3625 and 3682 cm⁻¹), which remained at all WO_x loadings. Based on WO_x/ZrO_2 samples prepared using incipient wetness impregnated Degussa ZrO₂, Vaidyanathan et al. attributed the lower-wavelength IR peaks to bridging OH groups (Zr–OH–Zr). They concluded that the WO_x species preferentially bonded to the ZrO₂ surface through the isolated OH groups rather than the bridging OH groups, implying incomplete coverage of the underlying support [57]. However, it cannot be ruled out that the bridging OH groups are located below the surface and not accessible to the WO_x surface species, as suggested by proton nuclear magnetic resonance (NMR) studies of alumina-supported metal oxides by Mastikhin et al. [58,59].

Still, other data indicate that the ZrO₂ surface is exposed, even at surface coverages >7.8 W/nm². Through combined low-temperature CO chemisorption (CO adsorbs on coordinately unsaturated Zr cations) and ion scattering spectroscopy (with a surface sensitivity of 0.3 nm), Vaidyanathan et al. reported that, for samples prepared through impregnation of crystalline ZrO₂, surface coverage increased approximately linearly, up to a WO_x loading of 1.7 wt% (or 1.2 W/nm²) and reached a plateau of ~54% above 6 wt% (or 4.6 W/nm²) [57,60]. Ferraris et al. [61] found a very similar trend for materials prepared through ion-exchange and incipient wetness impregnation (Figure 2.2[a]). Scheithauer et al. [56] presented CO adsorption/FTIR data suggesting that coordinatively unsaturated Zr (Lewis acid) sites were present at surface densities as high as 14.1 W/nm².

Using benzaldehyde as a selective probe molecule for the basic sites of ZrO_2 , Naito et al. [48] reported that there was near-100% coverage of ZrO_2 by WO_x species at 4 W/nm² for materials calcined at 650°C. However, for materials calcined at a lower temperature of 300°C, they found that ~55% coverage by WO_x was measured at 4 W/nm²; full surface coverage was not reached until 10 W/nm²



FIGURE 2.2 WO_x surface coverage of WO_x/ZrO₂ determined from (a) CO chemisorption at 77 K (The [×] marks are data from Vaidyanathan et al. [60]. Taken from Ferraris, G., De Rossi, S., Gazzoli, D., Petliti, I., Valigi, M., Magnacca, G., and Morterra, C., *Appl. Catal. A: Gen.* 2003, *240*, 119–128. With permission.) and (b) benzaldehyde chemisorption at 250°C (The open and closed symbols represent samples calcined at 300 and 650°C, respectively. Taken from Naito, N., Katada, N., and Niwa, M., *J. Phys. Chem. B* 1999, *103*, 7206–7213. With permission.)

(Figure 2.2[b]). Materials with the same surface density ρ_{surf} values can thus have different coverages of the ZrO₂ surface, highlighting the notion that monolayer coverage by the supported layer does not necessarily correspond to a completely inaccessible support.

2.4.2 Molecular Structure of WO_x Species

Wachs and coworkers prepared WO_x/ZrO₂ with different WO_x loadings through incipient wetness impregnation, using Degussa ZrO₂ (mixture of monoclinic and tetragonal crystal phases, 39 m²/g) and ammonium metatungstate. Samples exhibited a sharp Raman band in the ~1000 to 1010 cm⁻¹ region, which is due to a stretching mode of a terminal tungsten oxo (W=O) bond (Figure 2.3). The broader Raman bands at 804 and 875 cm⁻¹ were attributed to W–O–W bonds, indicating that polytungstates coexist with monotungstates below monolayer coverage. Direct quantification of the distribution of these species and WO₃ crystals through Raman spectroscopy is not possible, since the Raman signals for the polytungstates (and polymerized metal oxide species, in general) are very weak [25,62].

Monotungstates have only one W=O oxo bond under dehydrated conditions, according to oxygen isotope exchange studies [63]. The tungsten center is



FIGURE 2.3 In situ Raman spectra taken after dehydrating the materials (previously calcined) at 500°C. The weight loadings of 1, 3, and 5% correspond to 0.7, 2.1, and 3.5 W/nm², respectively. For reference, crystalline WO₃ has sharp and intense bands at ~715 and ~ 800 cm⁻¹ (Taken from Kim, D.S., Ostromecki, M., Wachs, I.E. J. Mol. Catal. A: Chem. 1996, 106, 93–102. With permission.)

coordinated totally to six oxygens in distorted octahedral symmetry, as indicated by EXAFS and CO adsorption/FTIR studies [46,47,56,61,64]. Thus, isolated WO₆ octahedra presumably bind to the zirconia support through five W–O–Zr bonds. Polytungstates are oligomers of WO₆, which connect via W–O–W linkages (Figure 2.4). The number of WO₆ units, extent of connectivity, and physical dimensions of a polytungstate domain are not known and cannot be quantified yet [47].

2.4.3 Relationship Between WO_x Surface Structure and Catalytic Properties

An understanding of how the molecular structure of WO_x relates to observed catalytic properties has increased since Hino and Arata's work. In their report, they calcined their impregnation-derived WO_x/ZrO₂ samples at several temperatures (Table 2.3), and found that those calcined at 800 and 850°C were the most active for pentane isomerization [30]. The tungsten content was ~13 wt%; no surface areas were reported, and the surface densities could not be calculated.



FIGURE 2.4 Schematic of (a) monotungstate and (b) polytungstate surface species

TABLE 2.3

Structural Properties of Two 825° C-Calcined WO_xZrO₂ Materials Prepared by Santiesteban *et al.*

Preparation method	Surface area (m ² /g)	WO ₃ content (wt%)	ρ _{surf} (W/nm ²)	Strong Brønsted site amount	
				(meq/g)	Site/nm ²
Impregnation of refluxed Zr(OH) ₄	62	21.3	8.9	0.002	0.019
Co-precipitation	62	19.5	8.2	0.0039	0.037
Source: Calculation Han S Ba	s are based on va	alues taken i Chang CI	from Santiest	eban, J.G., V 997 <i>16</i> 8 43	Vartuli, J.C.,

They concluded that the active (super)acid sites were generated from the crystallization of the amorphous $Zr(OH)_4$ support into the tetragonal phase, though they did not comment on the molecular nature of the active sites [65].

Mobil (now ExxonMobil) researchers compared WO_x/ZrO_2 materials prepared through impregnation and co-precipitation for pentane isomerization [42]. By titrating the Brønsted acid sites with 2,6-dimethylpyridine and examining the catalytic activity of the poisoned samples, they determined that the impregnated and co-precipitated WO_x/ZrO_2 samples had a similar amount of total Brønsted acid sites (~0.0094 meq/g, or ~0.09 site/nm²). However, the latter contained twice as many strong Brønsted sites active for pentane isomerization (Table 2.3). Co-precipitation led to a more active material due to a higher surface density of strong Brønsted sites, though the strong Brønsted site amount did not appear to be related to tungsten surface density. They reported a maximum in isomerization activity as a function of tungsten oxide content in co-precipitated materials. This maximum activity behavior of WO_x/ZrO_2 was observed by others for *n*-butane isomerization [41,48].

Iglesia and coworkers [47,55,66] observed a similar maximum in reaction rates for *o*-xylene isomerization over WO_x/ZrO_2 . Like Hino and Arata, they observed that reaction rates (in terms of turnover frequencies or TOF's, normalized to total W content) were greatest in value at an intermediate calcination temperature (Figure 2.5[a]). WO_x/ZrO_2 samples with different tungsten loadings exhibited a different maximum in *o*-xylene TOFs as a function of calcination temperature. By accounting for surface areas at different calcination temperatures, they were able to collapse the reaction rates roughly onto a single volcano-shaped curve when plotted against W surface density (Figure 2.5[b]). They found that WO_x/ZrO_2



FIGURE 2.5 *o*-Xylene reaction rates over WO_x/ZrO₂ with different tungsten loadings plotted as a function of (a) calcination temperature and (b) tungsten surface density (Taken from Barton, D.G., Soled, S.L., Meitzner, G.D., Fuentes, G.A., and Iglesia, E., *J. Catal.* 1999, *181*, 57–72. With permission.)

exhibited similar catalytic behavior for 2-butanol dehydration in terms of initial TOF's [67].

Barton et al. [47,55] attributed the high reaction rates to the presence of polytungstates, as inferred from UV-Vis, x-ray diffraction (XRD), and Raman characterization results. Monotungstates and polytungstates are found at $\rho_{\text{surf}} < 4 \text{ W/nm}^2$, and crystalline WO₃ species are detected through XRD at $\rho_{\text{surf}} > 8 \text{ W/nm}^2$. In the intermediate range of 4 to 8 W/nm², polytungstates and crystalline WO₃ nanodomains (which cannot be detected through XRD but can be detected through Raman spectroscopy) are found. They suggested that the TOF increases with surface density and polytungstate population until ~ 10 W/nm², above which additional tungsten content contributes to the formation of WO₃ crystals containing inactive and inaccessible tungsten atoms. They proposed that polytungstates reduce to form bronze-like $WO_x^{\delta-}$ domains, charge balanced by spatially delocalized $H^{\delta+}$, or Brønsted acid sites (Figure 2.6). The polytungstates are reducible by hydrogen gas or by the reactant hydrocarbon (e.g., 2-butanol) during the reaction, and the ease in reduction increases with domain size [54]. Two important findings are noted: calcination temperatures above 800°C are not needed to yield active WO_x/ZrO_2 materials, and the reaction rates over WO_x/ZrO_2 depend solely on W surface density.

In their modification of incipient wetness impregnation, Knözinger et al. [46] prepared WO_x/ZrO_2 by refluxing a suspension of $Zr(OH)_4$ in an aqueous solution of ammonium metatungstate for 16 h, and then evaporating the suspension to dryness. After calcining at 650°C, these refluxed WO_x/ZrO_2 materials have surface densities that exceed the monolayer coverage of 4 W/nm² without the formation of WO₃ crystals (Table 2.4). One would expect that calcination temperatures above the Tammann temperature of bulk WO₃ (600°C) lead to sufficient mobility of the surface WO_x species for coalescence and crystallization to occur [68]. The calcination temperature of 825°C is sufficiently high to induce WO₃ crystal formation at most surface densities above 4 W/nm². The refluxing step apparently yields WO_x/ZrO_2 with polytungstates which are more thermally stable than impregnated materials; Scheithauer et al. [46,56] speculated the polytungstate domains



FIGURE 2.6 Proposed mechanisms for activation of polytungstate to form acid site (Taken from Baertsch, C.D., Soled, S.L., and Iglesia, E. *J. Phys. Chem. B* 2001, *105*, 1320–1330. With permission.)

TABLE 2.4 WO₃ content, surface area, and surface densities for WO_x/ZrO₂ calcined at 650 and 825°C

	WO _x /ZrO ₂ calcined at 650°C		WO _x /ZrO ₂ calcined at 825°C	
WO ₃ weight loading (wt%)	Surface area (m ² /g)	$ ho_{surf}$ (W/nm ²)	Surface area (m ² /g)	$ ho_{surf}$ (W/nm ²)
0	~30	0	~ 18	0
3.6	54	1.7	30	3.1
5.9	64	2.4	40	3.8
8.6	69	3.2	46	4.9
10.5	82	3.3	46	5.9 ^a
13.6	88	4.0	42	8.4 ^a
19.0	96	5.1	35	14.1 ^a
23.9	70	8.9	30	20.7 ^a
32.0	43	19.3	28	29.7 ^a

^a Raman bands for WO₃ crystals observed.

Source: Values taken from Scheithauer, M., Grasselli, R.K., and Knözinger, H. Langmuir 1999, 14, 3019–3029; Scheithauer, M., Cheung, T.K., Jentoft, R.E., Grasse R.K., Gates, B.C., and Knözinger, H., J. Catal. 1998, 180, 1–13.

to contain Zr cations in a heteropolyacid-like form. Kuba et al. [69,70] reported that pentane molecules formed radicals over polytungstate-containing WO_x/ZrO_2 under reaction conditions, leading to the reduction of W^{6+} to W^{5+} cations and the formation of hydroxyl groups. This redox initiation step may be responsible for the induction period observed in pentane conversion with time [56].

2.5 New Synthesis Approaches

The concept of polymerized WO_x surface species as the active sites for acid catalyzed molecular conversions upon partial reduction provides the motivation to learn how to control the molecular structure of these surface species more rationally at the synthesis level. The following synthesis routes have been reported for WO_x/ZrO_2 materials with desirable structural properties (such as high surface areas, high thermal stability, and controlled pore sizes) and may provide greater control over polytungstate formation with further study.

2.5.1 Surfactant Templating

Surfactant templating chemistry involves the hydrolysis and condensation of solubilized precursors of metal oxides in the presence of surfactant molecules that form the eventual pores in the inorganic matrix. Mobil (now ExxonMobil) researchers reported in 1992 that surfactants could be used to template highly ordered pore channels of uniform sizes in silicate structures (Figure 2.7) [71-84]. A solution of hexadecyltrimethylammonium bromide contains aggregates of surfactant molecules called micelles, and addition of a silicate precursor in basic solution causes immediate precipitation of an organic/inorganic mesostructure. Formation involves the electrostatic binding of negatively charged silicate oligomers to the positively charged ammonium head groups on the spherical micelle surface, the elongation of micelles into rods, the packing of the rods into a hexagonal array, and the condensation of the silicate between the rod-shaped micelles. The mesostructure is calcined to remove the surfactant, thereby creating a honeycomblike structure. The resulting mesoporous silica material has high surface areas (>1000 m²/g); uniform pore sizes (2 to 10 nm); liquid crystal-like, long-range ordering of the pores, and high thermal stability (>800°C). Materials with larger pore sizes can be prepared using longer surfactant molecules, organic liquids to swell the micelles, and amphiphilic polymers.

Surfactant templating chemistry can be extended to many nonsilicate compositions after modifications to the synthesis route. These materials are less structurally stable than the mesoporous silicates, which is attributed to the thinness of the amorphous pore walls (\sim 1 to 2 nm). Stucky and coworkers [85,86] showed that this problem could be mitigated by preparing the materials with thicker walls. To prepare mesoporous WO₃, they dissolved a poly(ethylene oxide)– poly(propylene oxide)–poly(ethylene oxide) triblock copolymer and WCl₆ salt in ethanol, and dried the resulting solution in open air. The tungsten salt reacted with moisture to undergo hydrolysis and condensation reactions. These chemical reactions caused the eventual formation of amorphous WO₃ around triblock copolymer micelle-like domains, and after calcination at 400°C, a mesoporous WO₃ with thick, nanocrystalline walls (\sim 5 nm) and surface area of 125 m²/g was formed.

A mesoporous WO_x/ZrO_2 was prepared in an analogous fashion, in which $ZrCl_4$ salt was added with WCl_6 prior to drying of the ethanolic solution [85]. After calcination at 400°C, the resulting mesoporous material was amorphous, with a pore wall thickness of 4.5 nm and a surface area of $170 \text{ m}^2/\text{g}$. The distribution of W and Zr atoms was not reported, although the W can be presumed to be distributed on the surface and throughout the pore walls.



FIGURE 2.7 Illustration of two-step preparation of hexagonally ordered mesoporous silica MCM-41

2.5.2 NP Surfactant Templating

Wong et al. [87] reported the use of metal oxide NPs in surfactant templating, which allowed the synthesis of tungstated zirconia, tungstated titania, and tungstated alumina. In the preparation of WO_x/ZrO_2 , a clear suspension of ZrO_2 NPs (diameter ~ 3 to 10 nm) is added to a solution of ammonium metatungstate and (ethylene oxide)₂₀–(propylene oxide)₇₀–poly(ethylene oxide)₂₀ triblock copolymer, which leads to immediate precipitation. It is thought that the metatungstate anion binds to the surface of the positively charged NPs, and the coated NPs aggregate around the polymer micelles (Figure 2.8).

Calcination of the dried precipitate at 600°C removes the organics from the inorganic framework and transforms the metatungstate into WO_x surface species. The resulting material has a surface of 130 m²/g, a pore size in the 4 to 6 nm range, and a pore wall thickness of ~4 to 6 nm (Figure 2.9). There are no crystalline phases of ZrO₂ or WO₃, as characterized through XRD. The material does not crystallize into distinct ZrO₂ and WO₃ crystal phases until heated above 700°C.

The use of ZrO_2 NPs ensures that the WO_x species are on the surface. With a WO₃ content of ~30 wt%, the surface density is calculated to be 6 W/nm².



FIGURE 2.8 Illustration of two-step preparation of NP/surfactant-templated tungstated zirconia



FIGURE 2.9 TEM image of NP/surfactant-templated WO_x/ZrO_2 (calcined at 600°C)

NP/surfactant-templated WO_x/ZrO₂ contains no crystalline WO₃ according to *in situ* laser Raman spectroscopy [88,89]. It is hypothesized that the ZrO₂ NPs stabilize polytungstates from crystallizing by trapping them in the gaps between adjacent NPs, allowing for the high content of amorphous WO_x. Some batch-to-batch variation is observed due to sensitivity of the final structure to synthesis conditions, which affects the WO₃ content, surface area, and surface density (as high as 12 W/nm²).

2.5.3 Modified Sol–Gel Chemistry

To reduce the variability in the final structure, a new synthesis strategy involving sol-gel chemistry is being studied. Knowles et al. [89] posited that, if ZrO₂ NPs act to stabilize polytungstates by entrapment in the NP gaps, then a network of ZrO_2 NPs would also stabilize WO_x in a similar fashion. A zirconia gel prepared from the gelation of a zirconium alkoxide-derived sol is one such example of an NP network. This gel was prepared through controlled hydrolysis of zirconium *n*-propoxide, and subsequently mixed with a solution of ammonium metatungstate. To avoid catastrophic pore collapse upon drying to form a xerogel, ascorbic acid was added to the mixture. This organic is thought to bind to the gel surface and to prop up the internal gel framework during drying. Calcination at 600°C led to mesoporous WO_x/ZrO₂ with an open structure similar to that of NP/surfactanttemplated WO_x/ZrO₂ (Figure 2.10). XRD and Raman spectroscopic data indicate the presence of tetragonal ZrO_2 with grain sizes ~16 nm and the absence of WO₃ crystals for a WO_x/ZrO_2 with 10.6 W/nm². This two-step gelation method allows the WO₃ content of the final material to be controlled independent of the support formation, unlike NP/surfactant templating, which require the simultaneous presence of metatungstate and ZrO₂ NPs.



FIGURE 2.10 TEM image of sol-gel-derived WO_x/ZrO_2 (calcined at 600°C)

The two forms of NP-supported WO_x/ZrO_2 materials (prepared from NP/surfactant templating and sol–gel chemistry) are active for the dehydration of methanol to dimethylether [89], according to methanol oxidation studies [90,91]. It is hypothesized that these NP-supported materials contain a larger amount of polytungstates than conventionally prepared WO_x/ZrO_2 and therefore are more active [89].

Boyse and Ko [45] prepared WO_x/ZrO₂ through a one-step co-gelation (Table 2.2). An acidic alcoholic solution of zirconium *n*-propoxide and ammonium metatungstate was prepared, which gelled in \sim 1 min. The resulting gel was supercritically dried in CO₂ to remove the solvent without collapsing the pore structure. Calcination led to a material with mesopores in the range of 10 to 20 nm. The co-gelled WO_x/ZrO₂ contained more thermally stable WO_x species compared with the impregnated material. As in the case of co-precipitated supported metal oxides, it could not be ruled out that tungsten atoms were trapped within the ZrO₂ support.

Signoretto et al. [92] reported a one-step co-gelation method, in which zirconium *n*-propoxide and tungsten *n*-propoxide was combined with nitric acid, water, and isopropanol to create a homogeneous solution that gelled overnight. Supercritically dried in CO_2 and calcined, the final material was found to contain more entrapped tungsten than those prepared with zirconium *n*-propoxide and ammonium metatungstate.

In a very different approach, Melezhyk et al. [93] prepared gel-like particles using zirconyl chloride and ammonium metatungstate. A solution of the two salt precursors and a solution of poly(vinyl alcohol) were prepared at 100°C, and after combining, the resulting mixture was diluted with a buffer solution to yield transparent gel particles. These particles were carefully dried and calcined. By calcining the particles under inert atmosphere before calcining in air, higher surface areas could be achieved. This pyrolysis step converted the poly(vinyl alcohol) into carbonaceous residue that kept the framework from collapsing. The poly(vinyl alcohol) also acted as a porogen during gel formation and drying processes, which resulted in 10 nm pore sizes.

2.6 CONCLUSIONS

The challenge of controlling the nanostructure of WO_x/ZrO_2 , namely the molecular surface structure and the nanometer-scale framework properties, can be generalized to supported metal oxides. It is currently addressed through the development of new material synthesis chemistries, such as surfactant templating and sol–gel chemistry. Surfactant templating leads to relatively unstable porous materials, but thicker pore walls through a different chemistry or using NPs overcomes this problem. This method and sol–gel chemistry can lead to mixed metal oxides but the active metal oxide could be trapped below the support surface. Here, too, the use of NPs (either preformed or formed *in situ*) is a solution, by ensuring the localization of the active phase on the support surface. It appears that NPs in

the form of a porous framework can stabilize the active phase as thermally stable polymeric surface species, providing a new and interesting type of nanostructured supported metal oxide. Ultimately, the ability to engineer the catalyst structure at the nanoscale and the fundamental understanding of the synthesis–structure– property relationships of supported metal oxides will further enable the rational design and preparation of supported metal oxides.

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3 Defect Chemistry and Transport in Metal Oxides

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3.1 INTRODUCTION

Heterogeneous catalysis occurs at the surface of solids. To describe the overall catalytic process it is obvious that one must consider fluid-phase transport of reactants to, and products away from, the solid surface. However, it is also true that, in the case of oxide materials, solid-phase transport of defects must be considered if we are to have a full description of the processes occurring at the surface. Furthermore, such defects, when present at the surface of the oxide, play a very important role in determining the catalytic activity of the solid. The nature of these surface defects is strongly related to the bulk defect chemistry of the solids. In this chapter we describe the bulk defect transport and electrical conductivity. We conclude the chapter by looking at the use of oxide membranes in chemical reactors. Such membranes rely upon the ability of the oxide material to selectively transport defects which themselves undergo catalytic reactions at the free membrane surfaces. We focus on the versatile perovskite family of metal oxides which exhibits both ionic and electronic conductivity (pure ion conductors or solid electrolytes are dealt with elsewhere in this book).

3.2 TYPES OF DEFECTS

In an ideal ionic crystal, each atom is located at its regular lattice site and all sites are occupied, however, due to entropy considerations all real crystals deviate from the perfect atomic arrangements. Important physical properties of a metal oxide such as electrical transport, diffusion and diffusion-controlled processes such as sintering and phase separation, catalytic activity, melting point and various optical properties depend on the presence of defects. Numerous types of lattice defects are recognized: electrons and positive holes, excitons (excited electrons that are accompanied by their holes), vacant lattice sites and interstitial atoms, impurity atoms in interstitial or substitutional positions, dislocations and stacking faults. In addition to these primary imperfections, there are transient imperfections such as electromagnetic quanta and charged and neutral radiation. For convenience, we will concentrate on atomic defects and some electronic defects; however, it is important to understand that all different types of imperfections interact among themselves.

3.2.1 Point Defects

Point defects are missing, substituted or interstitial ions and occur in all crystalline materials. They are electronically charged and can be intrinsic or extrinsic. Intrinsic point defects are thermally generated in a crystal, whereas extrinsic defects are formed by the addition of an impurity or dopant.

The most common types of intrinsic point defects are Schottky and Frenkel defects (Figure 3.1). A Schottky defect consists of a vacant cation lattice site and a vacant anion lattice site. To form a Schottky defect, ions leave their normal lattice positions and relocate at the crystal surface, preserving overall charge neutrality. Hence, for a metal monoxide, MO, vacant sites must occur equally in the cation and anion sublattice and form a Schottky pair, whereas in binary metal oxides, MO₂, a Schottky defect consists of three defects: a vacant cation site and two vacant anion sites. A Frenkel defect forms when a cation or anion is displaced from its regular site onto an interstitial site, where, the resulting vacancy and interstitial atom form a Frenkel defect pair.

The presence of Schottky defects lowers the overall density of the material because the volume is increased at constant mass. Frenkel defects do not change the volume and the density of the material therefore remains the same. Hence, density measurements can be a useful tool for assessing the type of defect disorder in oxides if the defect content is high enough.



FIGURE 3.1 Formation of Schottky and Frenkel disorders in an ionic crystal

During thermal activation of an intrinsic defect in a lattice, the amplitude of lattice vibrations is increased and, subsequently, atoms become more likely to be displaced off their regular sites. The concentration of point defects is in thermal equilibrium with the crystal, given by:

$$G = G_0 + n\Delta g - T\Delta S_c \tag{3.1}$$

where G is the free energy of the crystal upon forming n defect pairs, each defect pair consuming an energy Δg during formation, and ΔS_c is the configurational entropy of the crystal. The change in free energy is therefore:

$$\Delta G = n\Delta g - T\Delta S_{\rm c} = n\Delta g - Tk\ln P \tag{3.2}$$

with *P* being the probability or the number of possible ways in which the defect can be arranged. For instance, *N* Frenkel pairs consist of n_i interstitials and n_v vacancies. Since the defects are formed in pairs, $n = n_i = n_v$, the configurational entropy is given by:

$$\Delta S_{\rm c} = k \left(\frac{N!}{(N-n_{\rm v})!n_{\rm v}!} \right) \left(\frac{N!}{(N-n_{\rm i})!n_{\rm i}!} \right) = 2k \ln \left(\frac{N!}{(N-n)!n!} \right) \tag{3.3}$$

The Stirling approximation, $\ln N! = N \ln N - N$, can be applied for large numbers of *N* and *n*, giving:

$$\Delta S_{\rm c} = 2k[N\ln N - (N-n)\ln (N-n) - n\ln n]$$
(3.4)

When Equation (3.4) is substituted for ΔS_c in Equation (3.2), the total free energy is given by:

$$\Delta G = n\Delta g - 2kT \left[N \ln\left(\frac{N}{N-n}\right) + n \ln\left(\frac{N-n}{n}\right) \right]$$
(3.5)

and, when the derivative $(\partial \Delta G / \partial n)_{T,P} = 0$, is evaluated with $(N - n) \sim N$ for dilute defects, the concentration of defects is given as:

$$\frac{n}{N} = \exp\left(-\frac{\Delta g}{2kT}\right) = \exp\left(-\frac{\Delta s}{2kT}\right) \exp\left(-\frac{\Delta h}{2kT}\right)$$
(3.6)

The entropy, Δs , is the nonconfigurational entropy that is associated with lattice strains and changes in vibrational frequencies and is much less than the configurational entropy. The most significant conclusion from relation (3.6) is that the defect concentration depends exponentially on the formation of free energy, Δg , and on temperature, *T*.

Point defect equilibria can be described with the "concept of defect pairing," however this concept only applies to materials with low concentrations of defects, <1%, where interactions between defects may be ignored and the defects may be considered as randomly distributed. In the concept of defect pairing, ω_{vv} is the energy of interaction between a pair of cation vacancies and ω_{ii} the energy of interaction between a pair of cations. If ω_{vv} and ω_{ii} are negative, then the defects exert an attractive force on each other and there is a tendency to form groups or clusters, which, if sufficiently large, will nucleate a new phase. At a critical composition, the crystal structure will break up into two phases (=saturation of a solution with a solute).

At higher defect concentrations, however, when substantial defect interactions are involved, the concept of point defects is mostly inadequate to explain nonstoichiometry. Large deviations from stoichiometry are accommodated by the formation of clusters of point defects and alternative models involve ordering of point defects to give rise to planar faults or new structural features, which eliminate point defects.

Defects and defect chemical equations are best described using a standard notation, the Kröger–Vink notation [1,2], which contains three parts: the main body identifies whether the defect is a vacancy "V" or an ion such as "Al." The subscript denotes the site that the defect occupies which is either a regular lattice site or an interstitial site, *i*. The superscript indicates the effective charge of the defect relative to the perfect crystal lattice; a dot represents a positive charge and a dash a negative charge whereas an × is used to indicate neutrality. For instance, $V_{AI}^{//}$ is a vacant aluminium site that has a triple negative effective charge and AI_{Mg}^{\bullet} is an aluminium atom at a magnesium site with a positive effective charge relative to the perfect lattice. The Frenkel reaction for the system AgCl can be written using the Kröger–Vink notation as: $Ag_{Ag}^{\times} \rightarrow Ag_i^{\bullet} + V_{Ag}^{\prime}$, indicating that a silver atom located at its regular site moves to an interstitial site giving a positive effective charge and subsequently generating a vacancy at its regular site that is negatively charged.

Extrinsic defects are formed not only by the presence of impurities or introduction of dopant or solutes into the metal oxide but also by oxidation or reduction processes. Whether a defect structure is considered as intrinsic or extrinsic depends on the relative concentration of intrinsic and extrinsic defects,