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Niobium Compounds: Preparation, Characterization, and Application in Heterogeneous Catalysis

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I. Introduction

Niobium chemistry is not widely known despite increasing interest in the application of niobium compounds within many fields. Niobium materials are presently of great interest in heterogeneous catalysis where they are used as catalyst components or are added in small amounts to catalysts. The growing focus on niobium catalysts has led to international conferences devoted mainly or exclusively to the chemistry and catalysis of niobium within the past decade. These conferences in turn resulted in interesting review papers by Tanabe in 1990[1] and Tanabe and Okazaki in 1995[2] that primarily describe the catalytic application of niobium compounds.

This review presents a broader view of niobium chemistry including many aspects of the preparation, structure, and physicochemical and catalytic properties of niobium compounds as well as their applications. The characterization of the niobium compounds is very important to the discussion of their catalytic activity and for the prediction of both their activity and selectivity in various reactions. Thus, the characterization of niobium, niobium oxides, phosphates, molecular sieves containing niobium (zeolites, mesoporous materials of MCM-41 type, mesoporous oxides), and other niobium compounds such as oxynitrides, carbides, and sulfides is covered in this paper. In addition, one section is devoted to the application of these compounds in heterogeneous catalysis. This review is based mainly on the literature from 1990 to the present. About half of the included papers were published after the last review,[2] while many others were not included in the previous review articles.[1,2]

II. Niobium: Existence, Physicochemical Properties, and Noncatalytic Application

Niobium (Nb), named after Niobe, a daughter of Tantalus, and also previously called columbium (Cb), after the American Columbia, was discovered in 1801 by Hatchett in an ore sent to England from Massachusetts.[3] The name niobium was officially adopted by IUPAC in 1950.

The abundance of niobium in the Earth's crust is 20 ppm. Niobium does not occur in a free state and is usually found together with tantalum in the mineral, $(Fe,Mn)M_2O_6$ (M = Nb, Ta). This mineral is known as columbite or tantalite, depending on which metal predominates.[4] The principal niobium-producing countries are Brazil, which accounts for about 60% of its total production, Canada, Nigeria, and Zaire. Niobium is mononuclidic, and its only natural isotope is ^{93}Nb.

In 1955, Kouzmenko and Kazakova[5] described a mineral nenadkevichite from Lovazero (Russia) that

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Maria Ziolek received her M.Sc. in chemistry in 1971 from Adam Mickiewicz University (AMU) in Poznam, Poland, where she also obtained a Ph.D. in physical chemistry in 1976. She received a postdoctoral training at the Fritz Haber Institute of Max-Planck Society in Berlin. In 1985, she was awarded the degree of D.Sc. (habilitation) for the research on the catalytic transformation of sulfur compounds. She has a long-standing collaboration with the catalytic and spectroscopic groups of the Fritz Haber Institute, Germany (with Dr. Hellmut G. Karge), and URA.CNRS.0414-ISMRA, Caen, France (with Dr. Jean-Claude Lavalley). In 1991–1996, she was a dean for students affair at the Faculty of Chemistry, AMU. Nowadays she is a professor and the Head of the Department of Heterogeneous Catalysis at the Faculty of Chemistry, AMU. Her research interests include heterogeneous catalysis, particularly concerning zeolites, metal oxides, and mesoporous molecular sieves catalysts, their synthesis, modification, characterization, and application. She has published 80 papers, 4 patents, and made 125 presentations at symposiums and conferences.

has the composition (Nb,Ti)$Si_2O_7 \cdot 2H_2O$. Rocha et al.[6,7] prepared and characterized a series of synthetic microporous analogues of nenadkevichite from Saint-Hilaire, Quebec (Canada), with Ti/Nb molar ratios ranging from 0.8 to 17.1. Their studies suggested that the niobium and titanium are coordinated in distorted octahedra.

Niobium has an atomic number of 41 and a relative atomic mass of 92.9064 and is a shiny, silvery metal with a typical metallic bcc structure.[8] When very pure, it is comparatively soft and ductile, but impurities make it harder. These properties are expected given niobium's position adjacent to the group IVA elements. Niobium is slightly less electropositive and smaller than its predecessor in the periodic table, while it is virtually identical in size to the heavier Ta as a consequence of the lanthanide contraction. The extra d electron appears to contribute to stronger metal−metal bonding in the bulk metals, leading to a higher melting point, boiling point, and enthalpy of atomization upon proceeding from the group IVA to the group VIA metals.[9]

Niobium, which belongs to group VA, is in many ways similar to its predecessors in group IVA.[4] It reacts with most nonmetals at high temperatures (fluorine reacts with niobium at RT, with chlorine and hydrogen at 473 K, and with nitrogen at 673 K), giving products that are frequently interstitial and nonstoichiometric, Niobium is resistant to most aggressive compounds and, thus, to corrosion. Due to its small thermal neutron capture cross-section and good resistance to several liquid−metal coolants such as sodium, lithium, etc., niobium is of major interest in nuclear technology.[4] In addition, it is used as an additive in many alloys and also acts as a grain refiner in structural steels, where it improves thermal shock resistance, hot ductility, and tensile strength. It is resistant to acids, including nitrohydrochloric (aqua regia), HCl, H_2SO_4, HNO_3, and H_3PO_4 and to many organic and inorganic compounds. Niobium is attacked by hot concentrated mineral acids, such as HF and HF/HNO_3 mixtures, but is resistant to fused alkali.

Although niobium exhibits all the formal oxidation states from +5 down to −1, its most stable state is +5. The +4 oxidation state is represented in halide compounds, while the +2 and +3 states appear in cluster compounds based on octahedral M_6X_{12} units.[4]

Niobium and some of its alloys exhibit superconductivity, making them of interest for high-powered magnets.[10] Although its corrosion resistance is not as outstanding as that of tantalum, its lower price and greater availability make niobium attractive for less exact uses such as linings in chemical plants.[4] Niobium is also widely used by the electronics industry in the manufacture of capacitors, where its oxide film is an efficient insulator, and as a filament or filament support.[4] Niobium carbide together with the carbides of other refractory metals as tantalum, titanium, tungsten, and vanadium is used as a hard carbide in cutting tools. Niobium also has been used in advanced air frame systems in space programs.[10]

Niobium is a component of some phosphate optical glasses and has been incorporated into thermocouples to increase their stability at elevated temperatures. Several metaniobates have been used in piezoelectric ceramics and dielectrics.[10] Its complete inertness to bodily fluids makes it an ideal component of bone implants and it also can be applied for internal suturing.[4]

Niobium-containing nonlinear optical materials, including $LiNbO_3$, $LiIO_3$, KH_2PO_4, are used as harmonic generators, frequency mixers, and parametric oscillators in the UV, visible, and near-IR regions. Another class of compounds [$K(Ta,Nb)O_3$, $BaNaNb_5O_{15}$, etc.] exhibit the properties of so-called electrooptic materials in which electric fields may be used to control light beams.[11]

III. Niobium Oxides

A. Nature and Physicochemical Properties of Various Niobium Oxides

Niobium(V) oxide is a white, air-stable, water-insoluble solid. It is much more stable and difficult to reduce than vanadium(V) oxide.[4,12] Nb_2O_5 is attacked by concentrated HF and dissolves in fused alkali. It may be described as amphoteric but is more characteristicly inert. Its structure is extremely complicated and displays extensive polymorphism, which will be described in the next section.[13]

Nb_2O_5 is probably comprised of NbO_6 octahedra connected by edges and corners. Since dissociation becomes discernible even at 1423 K, oxygen defects may be produced upon heating the Nb_2O_5 in a Bunsen flame. This results in a yellow form that reverts to Nb_2O_5 upon cooling in air.

High-temperature reduction (1073−1573 K) of Nb_2O_5 with hydrogen gives the bluish-black dioxide NbO_2 that has a distorted rutile structure and is diamagnetic. This reduction is reversible. The NbO_2 structure only exists when the oxygen ratio is maintained close to 2. Thus, an oxide of the composition $NbO_{2.09}$ shows X-ray diffraction lines that are characteristic of the pentoxide, even though it contains only a small excess of oxygen. NbO_2 is insoluble in water and is a very strong reducing agent in the dry state.[12]

Between Nb_2O_5 and NbO_2, there exists a homologous series of structurally related niobium oxide phases having the general formula $Nb_{3n+1}O_{8n-2}$ where $n = 5, 6, 7, 8$. In addition, oxides of formula $Nb_{12}O_{29}$ ($12Nb_2O_5{-}2O$) and $Nb_{94}O_{232}$ ($47Nb_2O_5{-}3O$), which are stoichiometrically related to Nb_2O_5, have been reported. These materials possess paramagnetic properties.[4]

Further reduction of Nb_2O_5 (1573−1973 K) produces the gray monoxide NbO that has a cubic structure and metallic conductivity but differs markedly from its vanadium analogue in that its composition ranges only from $NbO_{0.982}$ to $NbO_{1.008}$. The diffraction lines of NbO_2 begin to appear in $NbO_{1.04}$, while the oxides $NbO_{0.94}$ and $NbO_{0.87}$ show diffraction lines that are characteristics of the metal. The structure of NbO is a unique variant of the rock salt NaCl structure in which there are Nb vacancies at the eight corners of the unit cell and an O vacancy at its center (Figure 1). Therefore, the structure could be described as a vacancy-defect NaCl structure $Nb_{0.75 + 0.25}O_{0.75 - 0.25}$. However, since all the vacancies are ordered, it is better to consider NbO as having a new structure type in which both the Nb and O form four coplanar bonds. The central feature of this structure is a 3D framework of Nb_6 octahedral clusters (Nb−Nb 298 pm, cf. Nb−Nb 285 pm in Nb metal), which accounts for the metallic conductivity of the compound. The topological relationship between the NbO structure and SOD-type (zeolite) nets has been recognized.[14]

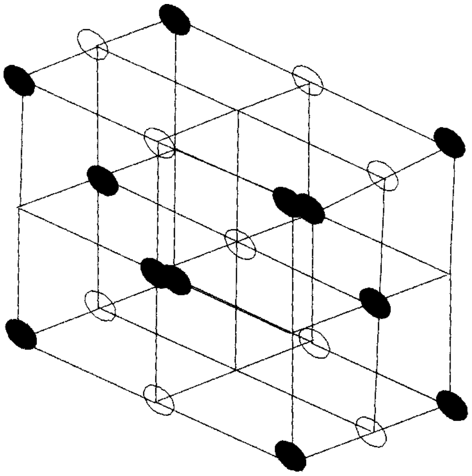


Figure 1. Crystal structure of NbO; (●) niobium, (○) oxygen.

The hydrated pentoxide (niobic acid) is obtained as a white precipitate with indeterminate water content when water-soluble complexes of the metal are hydrolyzed or when a solution of niobate is acidified. It is most commonly prepared by fusing the anhydrous pentoxide with 5−10 times its weight of alkali-metal pyrosulfate or hydrogen sulfate. This forms a soluble sulfato complex that is then leached with sulfuric acid or with a solution of another complexing agent such as oxalic acid. The hydrous oxide is then precipitated by diluting and boiling the solution in sulfuric acid or by adding ammonia to the oxalic acid solution.[12] Niobic acid is an insoluble polymeric oxide, and it seems probable that polymerization takes place through the intermolecular elimination of water between units such as $Nb(OH)_5$ or $NbO(OH)_3$. Different types of niobium oxide ionic species [$NbO_2(OH)_4^{-3}$, $Nb_6O_{19}^{-8}$, $H_xNb_6O_{19}^{-(8-x)}$ ($x = 1, 2$, or 3), and $Nb_{12}O_{36} - 12$] exist in aqueous solutions, and the solution pH as well as the niobium oxide concentration determines the specific niobium ionic species present (Table 1).[15]

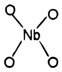
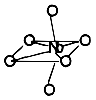
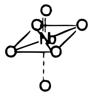
Table 1. Aqueous Niobiate Species at a pH Range from 14.5 to 0.55[a]

solution pH	species
>14.5	$NbO_2(OH)_4^{3-}$
14.5	$Nb_6O_{19}^{8-}$
11.5	$H_xNb_6O_{19}^{(8-x)-}$
6.5	$Nb_{12}O_{36}^{12-}$, $Nb_2O_5 \cdot nH_2O$
3.65	$Nb_{12}O_{36}^{12-}$, $Nb_2O_5 \cdot nH_2O$
0.55	$Nb_2O_5 \cdot nH_2O$

[a] Reproduced from ref 15. Copyright 1990 Elsevier Science.

Niobium oxide compounds generally possess an octahedrally coordinated NbO_6 structure that is distorted to different extents depending on whether its polyhedra are corner- or edge-shared. Occasionally, NbO_7 and NbO_8 structures can also be found in niobium oxide phases (Table 2). After the $Nb_2O_5 \cdot nH_2O$ precipitate is dried at 393 K for 2 h, it possesses

Table 2. Relationship between Niobium Oxide Structures and Raman Frequencies[a]

symmetry	type	Raman bands	compounds
	NbO_4	790-830 cm^{-1}	$YNbO_4$
	NbO_7 and NbO_8	500-700 cm^{-1}	Nb_2O_5 (amorphous; TT-, T-H-form) $LiNbO_3$ $NaNbO_3$
	NbO_6	850-1000cm^{-1}	Nb_2O_5 (H) $AlNbO_4$ $Nb(HC_2O_4)_5$

[a] Reproduced from ref 15. Copyright 1990 Elsevier Science.

features very similar to amorphous Nb_2O_5 in which there are slightly distorted NbO_6, NbO_7, and NbO_8 sites. In addition, $Nb_2O_5{\cdot}nH_2O$ also possesses a small number of highly distorted NbO_6 sites. The Nb^{5+} cation is very large and has difficulty fitting into an oxygen anion tetrahedron. Thus, only a few niobium oxide compounds (i.e., $YNbO_4$, $YbNbO_4$, $LaNbO_4$, and $SmNbO_4$) possess a tetrahedrally coordinated NbO_4 structure that is similar to the scheelite-like structure. Jehng and Wachs[15] also discovered that the interaction of niobium oxide with basic surfaces of a support results in the formation of highly distorted NbO_6 octahedra, while its interaction with acidic surfaces result in the formation of slightly distorted NbO_6, NbO_7, and NbO_8 groups. The dehydration process further distorts the already highly distorted NbO_6 octahedra due to the removal of coordinated water but does not perturb the only slightly distorted NbO_6 octahedra. The highly distorted NbO_6 octahedra possess Nb═O bonds and are associated with Lewis acid sites.[16] In contrast, the slightly distorted NbO_6 octahedra as well as the NbO_7 and NbO_8 groups only possess Nb−O bonds and are associated with Brønsted acid sites. Lewis acid sites are present in all supported niobium oxide systems, but the Brønsted acid sites are limited to the Nb_2O_5/Al_2O_3 and Nb_2O_5/SiO_2 systems.[15]

Hydrated niobium oxide ($Nb_2O_5{\cdot}nH_2O$; niobic acid) has a high acid strength ($H_o = -5.6{\sim}-8.2$). It remains bound to the support surface even in the presence of water and acts as an effective catalyst for reactions in which water molecules participate or are liberated.[17] It also has been reported[18,19] that the acidity of niobic acid increases upon treatment with sulfuric or phosphoric acid. Generally, hydrated niobium oxide crystallizes at 853 K, and its strong acid property disappears when it is heated to temperatures higher than 800 K.[20−22] To summarize, $Nb_2O_5{\cdot}nH_2O$ possesses both Lewis acid sites (which increase with increasing pretreatment temperatures up to 773 K and then decrease at higher temperatures) and Brønsted acid sites (which are most abundant at 373 K and decrease at higher temperatures) on its surface.[23]

Experiments performed by Fraissard et al.[24] showed that the theoretical number of protons per gram of hydrated niobium pentoxide at 573 K ($H_2Nb_6O_{16}$) is 1.6×10^{21}, which indicates that niobic acid contains two hydroxyl groups per unit cell. As the number of coordinated water molecules increases, the number of Brønsted acid sites (BAS) decreases, the concentration of hydronium ions (H_3O^+) increases, and the formation of $H_2O{\cdots}HO$ species is observed. In samples containing more than 2 water molecules per $H_2Nb_6O_{16}$, there are no longer any BAS, and the water molecules do not interact with the surface of the niobic acid. However, there is a linear correlation between the number of the adsorbed water molecules and the concentration of hydronium ions. The H_3O^+ concentration becomes constant when the number of adsorbed water molecules per BAS (n_{H_2O}/BAS) ≥ 5.3. The ionization coefficient is ca. 0.2 when $n_{H_2O}/BAS = 1$, so at this water content the acidity of niobic acid is comparable to that of NH_4Y (Si/Al = 2.4) and the dealuminated form of ammonium Y-type zeolite (Si/Al = 4.4). At saturated hydration, 50% of niobic acid's acid sites are ionized, revealing that only one of the two acid sites is particularly strong.

B. Niobium Oxide(V): Polymorphism

The amorphous niobium oxide(V) begins to crystallize in a "low-temperature" form called the ***T*** form (from the German "tief" for low) at about 773 K. Crystallization occurs more rapidly at higher temperatures until about 1103 K, where upon a transition to a "medium-temperature" (***M***) form becomes apparent.[12] This transition continues more rapidly at higher temperatures and heating for 4 h at 1273 K brings about a complete conversion. At even higher temperatures, a third transformation to a "high-temperature" (***H***) form has been reported.[12,25] These polymorphic transitions take place slowly, at temperatures which are not well-defined, and are irreversible. Some authors[26] have suggested that, although these three crystal modifications, (which have been re-designated as $\gamma = \boldsymbol{T}$, $\beta = \boldsymbol{M}$, $\alpha = \boldsymbol{H}$) exist, the β- and α-phases are essentially the same, and the transition therefore is to be regarded as occurring from γ to α. A further high-temperature metastable ϵ-phase has been observed to crystallize from molten Nb_2O_5 without supercooling and to transform spontaneously and exothermically to the α-modification at any temperature between 1103 and 1473 K. In fact, the only stable phase between 1103 and about 1673 K is the α-form. A low temperature δ-phase, which was mentioned in the paper of Frevel and Rinn,[27] was later shown to be a poorly crystalline variety of the γ-form.

H niobia (Figure 2) has a shear structure consisting of blocks of NbO_6 octahedra (3×4 and 3×5) that share corners with octahedra in their own block and edges with octahedra in other blocks.[28,29] One of the 28 Nb atoms in each unit cell is present in a tetrahedral site, which occurs at some block junctions, as depicted by the black circles in Figure 2.

The ***T*** phase has an entirely different structure, as shown in Figure 3. The unit cell contains 42 oxygen atom positions (large open circles). Eight of the Nb ions are present in distorted octahedra, while another eight Nb ions occupy pentagonal bipyramids.[29,30] The remaining 0.8 Nb ion per unit cell is located in interstitial 9-coordinated sites in the unit cell (small open circles).

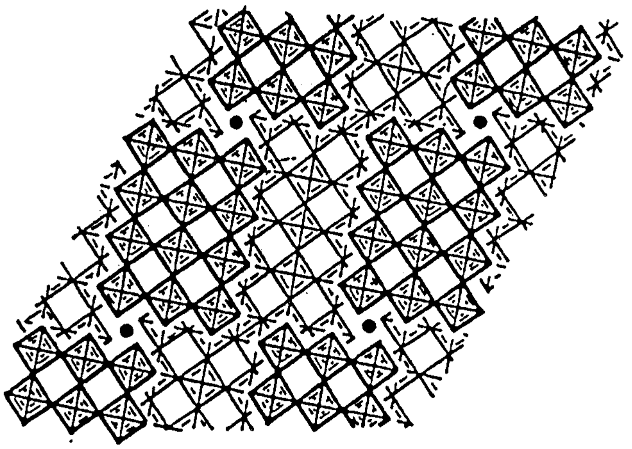


Figure 2. Crystal structure of ***H***-Nb_2O_5; (bold diamonds) NbO_6 octahedra, (●) Nb in tetrahedral site. (Reproduced with permission from ref 28. Copyright 1970 John Wiley & Sons Limited.)

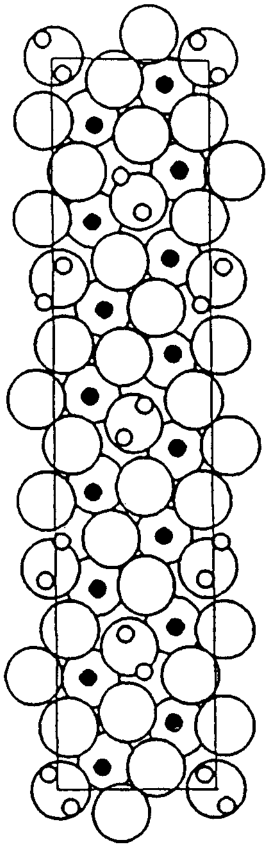


Figure 3. Projection of the structure of ***T***-Nb_2O_5 parallel to the [001] plane; (○) oxygen, (●, ○) niobium. (Reproduced with permission from ref 30. Copyright 1975 Munksgaard International.)

The principal polymorphs of stoichiometric Nb_2O_5 described above, ***T***(γ), ***M***(β), and ***H***(α), are obtained as polycrystalline products from the thermal treatment of pentoxide in contact with air or oxygen at varying temperatures. Single crystals of these polymorphs cannot be obtained from pure Nb_2O_5. However, they can be formed by chemical transport reactions in the presence of a halogen, usually chlorine, e.g.:[12]

$$Nb_2O_5(s) + 3NbCl_5(g) = 5NbOCl_3(g) \qquad (1)$$

After this initial step, the pentoxide is enclosed with a suitable amount of pentachloride and chlorine gas in a sealed tube that is maintained in a temperature gradient. By varying the upper and lower temperatures at the respective ends of the tube, it is possible to obtain well-formed single crystals of not only the previously known polymorphs, ***T***(γ), ***M***(β), and ***H***(α), but also of other forms. The primary new forms obtained possess a characteristic and well-defined X-ray powder diffraction pattern and have been designated ***B*** ("Blätter" (German) for leaflets or ζ), ***N*** (needles), and ***P*** (prism or η) in accordance with their crystal habit.[31]

Ko and Weissman concluded in their paper[32] that the many structures of bulk niobium pentoxide can be grouped into low-temperature and high-temperature forms, with the latter being more ordered. The crystallization behavior of niobium pentoxide, however, is influenced by the starting materials used, impurities that may be present, and any interactions with other components. These interactions are known to affect both the physical (mobility) and chemical (reducibility, acidity) properties of catalytic systems containing niobium pentoxide. Despite this variability, Nb_2O_5 crystallizes into a low-temperature form (***TT*** or ***T***) at ca. 773 K, a medium-temperature form (***M*** or ***B***) at ca. 1073 K, and a high-temperature form (***H***) at ca. 1273 K[32] when starting from an amorphous phase (Figure 4). The two low-temperature forms of Nb_2O_5, ***TT*** or ***T***, have long been thought to be the same, because (i) they have similar X-ray diffraction patterns (some reflections that are split in ***T*** niobia—orthorhombic—occur as one peak in ***TT*** niobia—monoclinic) and (ii) the ***TT*** phase does not always form from pure components as starting material. These observations suggest that ***TT*** may simply be a less crystalline form of ***T***, stabilized by impurities. The main differences are that some of the oxygen atoms in ***T*** are replaced by monovalent species (such as Cl^-) or vacancies—these being reported as impurities—in ***TT*** while the Nb atoms occupy a range of positions between two crystallographically similar

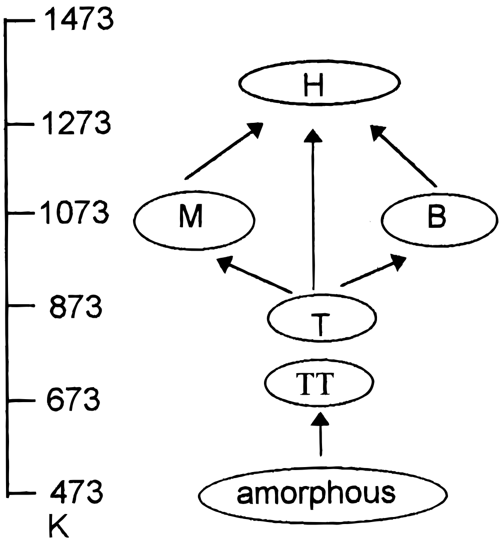


Figure 4. Polymorphism of Nb_2O_5. (Reproduced with permission from ref 32. Copyright 1990 Elsevier Science.)

sites. The structure of ***H***-Nb_2O_5 is highly ordered and consists of a sequence of blocks with (5 × 3) or (4 × 3) groups of corner-sharing NbO_6 octahedra within each block. ***M***-Nb_2O_5 has a related structure, while the structure of ***B***-Nb_2O_5 consists of rutile-like ribbons of edge-sharing NbO_6 octahedra.[33]

To summarize, there are many polymorphic phases of niobium pentoxide, i.e., ***TT***-, ***T***-, ***B***-, ***M***-, ***H***-, ***N***-, and ***P***-Nb_2O_5. The conversion of one form to another upon being heated in air is illustrated in Figure 5.[31]

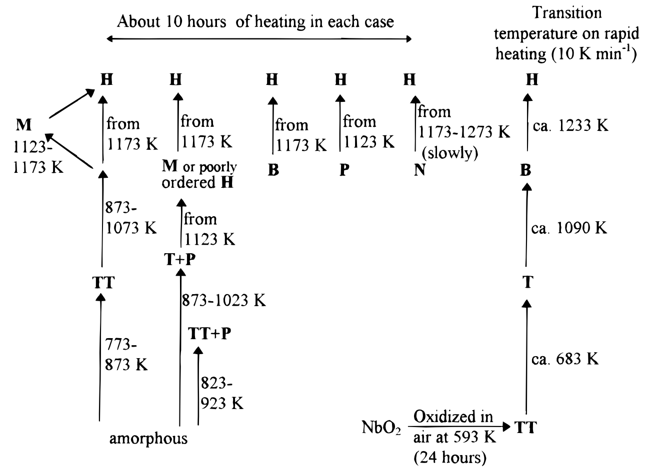


Figure 5. Interconversion of the various polymorphs of Nb_2O_5. (Reproduced with permission from ref 31. Copyright 1966 Wiley-VCH Verlag GmbH.)

IV. Niobium Phosphates

Niobium oxide, especially partially hydrated niobium oxide, is well-known as a valuable solid acid catalyst because of its strong surface acidity even in the presence of water.[17] However, the number of acid sites on the niobium oxide surface is relatively small, and the surface acidity is greatly decreased at higher temperatures (>700 K) due to the crystallization of the previously amorphous niobium oxide as the γ crystalline form. This decrease in acidity upon increasing the pretreatment temperature can be attributed to the transformation of protonic sites to Lewis acid sites with the elimination of water and to the loss of surface area. Okazaki et al.[34] have found that a H_3PO_4 treatment is effective for enhancing and retaining the surface acidity at higher temperatures. They also found that the crystallization can be inhibited by preparing niobium pentoxide with phosphoric acid. It is well-known that commercial niobium phosphate, which is amorphous, shows strong surface acidity and could promote some acid-catalyzed reactions.[35] Thus, niobium phosphate has a texture and acidic and catalytic properties similar to niobium oxide, but it has the advantage that it conserves these properties at higher pretreatment temperatures.[36]

Okazaki et al.[34] showed that amorphous niobium phosphate does not crystallize prior to 1073 K and exhibits high catalytic activity even after heat treatment at temperatures as high as 773 K. This material was prepared by the addition of H_3PO_4 to an aqueous solution of potassium niobate. Aging control and removal of the K^+ are important to enhancing the catalytic activity of the resultant niobium phosphate. This material also can be prepared by a one-step sol–gel synthesis followed by supercritical drying with carbon dioxide.[37]

Various types of amines can intercalate in the interlayer spaces of $NbOPO_4 \cdot nH_2O$.[38] Niobium phosphates that contain neutral acid molecules of H_3PO_4, H_2SO_4, and water in the interlayer spaces also have been prepared, but the acids were easily removed by washing with water. Layered acid niobium phosphate $Nb_2(OH)_2(HPO_4)(PO_4)_2 \cdot 4.4H_2O$ consists of two layers of $Nb(OH)_2PO_4$ connected by PO_4 groups, as if neutral H_3PO_4 intercalated into the layer spaces had condensed to link the layers.

Kinomura and Kumada[39] prepared an alkali metal niobium phosphate $NaNb_2(OH)_2(PO_4)_3 \cdot 2.5H_2O$ and an acid niobium phosphate $HNb_2(OH)_2(PO_4)_3 \cdot H_2O$. These compounds are isostructural, having a three-dimensional framework composed of $NbO(H_2O)(PO_4)$ layers connected by PO_4 groups. The sodium ions and protons are exchangeable with other alkali metal, alkaline earth metal, and alkylammonium ions. The acid niobium phosphate can also intercalate *n*-alkylamines. The PO_4 group that links the layers could be removed by ion exchange with certain ions and by intercalation with certain amines, and this transformed the three-dimensional (3D) structure into a layered structure.

Niobium phosphate bronzes (NPB), represented by $(K_3Nb_6P_4O_{26})_n \cdot KNb_2PO_8$, with $n = \propto$, which are analogous to the phosphate tungsten bronzes, have been reported by Benabbas et al.[40] The structure of this material is built up from NbO_6 octahedra and PO_4 tetrahedra.[41] The NbO_6 octahedra form infinite chains or layers by corner-sharing and are connected by PO_4 tetrahedra via corner-sharing to give low-dimensional structures (Figure 6). These are of interest because other compounds with quasi-low-dimensional structures, such as oxide bronzes, have interesting properties, including magnetic properties and superconductivity.

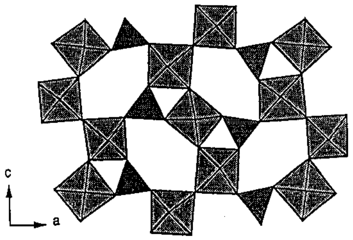


Figure 6. Layer of six-sided rings of NbO_6 and PO_4 polyhedra stacked along (010) in $K_3Nb_6P_4O_{26}$. (Reproduced with permission from ref 41. Copyright 1993 Elsevier Science.)

Niobium is also an effective promoter of $(VO)_2P_2O_7$ to form compounds of the type $((VO)_xNb_{1-x})_2P_2O_7$. These compounds retain the oxidizing ability of $(VO)_2P_2O_7$ and possess strong Lewis acid sites.[42]

V. Molecular Sieves Containing Niobium

A. Zeolites

Zeolites are natural or synthetic aluminosilicates with properties that make them very useful as heterogeneous catalysts, i.e., they have exchangeable cations (called extraframework cations) equivalent to the number of tetrahedral aluminum atoms in the network. Extraframework cations can be substituted by protons or other cations to result in changes to the zeolite's acidity. The zeolite pores (which may be one or more sizes) have diameters close to molecular dimensions (0.3−1.2 nm) depending on the size of the cation exchanged. Transition metals in different oxidation states and coordinations can be introduced into different zeolite structures either as charge-neutralizing cations, supported metal clusters, complexes, or lattice cations.

There is little information about the introduction of niobia into zeolite lattices. Because niobia salts are very sensitive to moisture, the traditional methods for modification of zeolites, specifically slurrying in aqueous solution, cannot be applied. Therefore, a solid-state interaction between niobia and a zeolite was explored as a method for Nb incorporation to zeolites. Thoret et al.[43] reported that Nb_2O_5 does not enter the zeolite, regardless of the reaction temperature or the composition of the mixture. Ziolek et al.[44,45] have stated no exchange of the Na^+ cations in NaY with niobium cations occurs during the heating of NaY with a Nb_2O_5 mixture at 975 K, whereas the exchange of cations does seem to occur on ammonium and dealuminated forms of zeolites. A decrease in the density of Brønsted acid sites and an increase in the density of Lewis acid sites were observed for the latter samples by IR spectroscopy following pyridine adsorption, TPD of ammonia, and 2-propanol decomposition.

The traditional procedure for cation exchange between NaY and an ethanol solution of $NbCl_5$ permits the replacement of Na^+ cations in the zeolite by niobium or niobium oxide species.[46] This conclusion is based on the following observations: (i) the removal of Na^+ from the zeolite lattice, (ii) the formation of a new phase registered by XRD and IR spectra, and (iii) an increase in 2-propanol and cumene conversion (see Table 3). These observations do not result when the exchange is attempted between NH_4NaY or DNH_4Y and a $NbCl_5$ solution.

Table 3. Cumene Transformation at 673 K[a]

catalyst	cumene conv. (%)	product distribution (%) propene	benzene	*n*-propyl benzene
NaY	3	2	4	90
NbNaY	61	51	47	2
$NbNaY-H_2O$	91	48	48	2

[a] Reproduced from ref 46.

Chang et al.[47] reported that a Nb-containing ZSM-5 zeolite was prepared by the impregnation of H-ZSM-5 or Na-ZSM-5 with a freshly prepared aqueous solution of niobium oxalate. They believe that Nb^{5+} is the charge balancing cation in the zeolite. Niobium-containing zeolites that have structures isomorphous with that of ZSM-5 were first reported by Saxton and Zajacek.[48] Molecular sieves containing niobium isomorphously substituted in their framework lattice were obtained by hydrothermal crystallization using quaternary ammonium templates.

A novel niobium silicate molecular sieve of MFI topology, designated as NbS-1, was synthesized hydrothermally and characterized by ESR and other physical methods.[49] γ-Irradiation of activated NbS-1 led to the formation of two radiation-induced hole centers (V centers) located on Si−O−Si and Nb−O−Si units of the framework, as identified by ESR. The Nb−O−Si unit can be deduced from a 10-line hyperfine structure attributable to ^{93}Nb ($I = 9/2$, 100% abundance). This provides convincing evidence for the incorporation of Nb into the silica framework.

A zeolite ZSM-5-supported oxide (5 wt %) was prepared from a niobium pentachloride methanol solution and was dried and calcined at 773 K as reported by Wierzchowski and Zatorski.[50]

Recently, the synthesis of a microporous framework niobium silicate displaying zeolite-type properties and containing niobium in octahedral coordination was reported by Rocha et al.[51] The novel material denoted AM-11 (Aveiro-Manchester microporous solid no. 11) was prepared from niobium oxalate and tetraethyl orthosilicate by autoclaving a mixture of these materials at 473 K for 15 days.

Niobium can play an active role in the stabilization of Cu-ZSM-5.[52,53] The addition of niobia also can decrease the number of aluminum atoms eliminated from the lattice of NH_4-ZSM-5 during its thermal treatment.[54]

B. Mesoporous Niobium Silicates of MCM-41 Type

In 1992, the hexagonally packed mesoporous materials prepared by Mobil[55] were confined to the silica- and aluminosilica-based MCM-41 family. These molecular sieves are formed by a mechanism in which surfactant liquid−crystal phases are believed to serve as templates (Figure 7). The structure and pore dimensions of MCM-41 materials are highly dependent on the properties of the surfactant, which supports this templating mechanism, but other phases including a cubic phase could also be achieved in the same manner. The diameter of these pores can be tuned between 0.2 and 10 nm by varying the length of the hydrophobic part of the surfactant. After calcination, these mesostructured materials exhibit ordered arrangements of the pores. These materials are not crystalline, and so their pore-size distributions are not as narrow as those of the microporous substances (zeolites). Their utility is due to their large, uniform pore sizes, which allow sterically hindered molecules to diffuse, and to their regular pore structures, which can serve as supports for conductive and magnetic materials.

A mesoporous niobium-containing silicate of the MCM-41 type was prepared for the first time by Ziolek et al.[56] Sodium silicate and niobium oxalate were utilized as silicon and niobium sources, respectively, and cetyltrimethylammonium chloride was used as a surfactant. The gel that formed from these components was loaded into a stoppered PP bottle and heated at 373 K for various lengths of time. The best material was obtained after heating for 48 h.

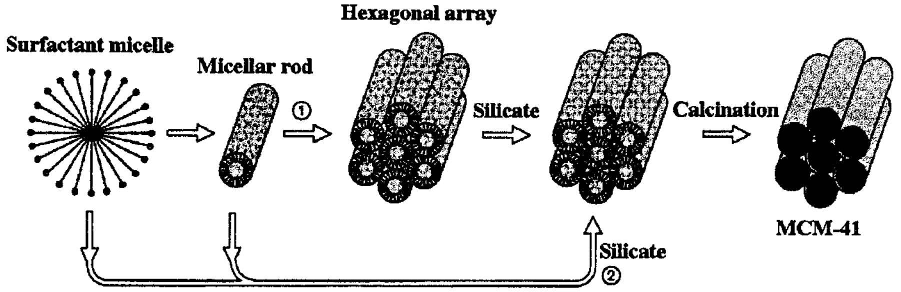


Figure 7. Possible mechanistic pathways for the formation of MCM-41: (1) liquid crystal phase initiated and (2) silicate anion initiated. (Reproduced with permission from ref 55. Copyright 1992 American Chemical Society.)

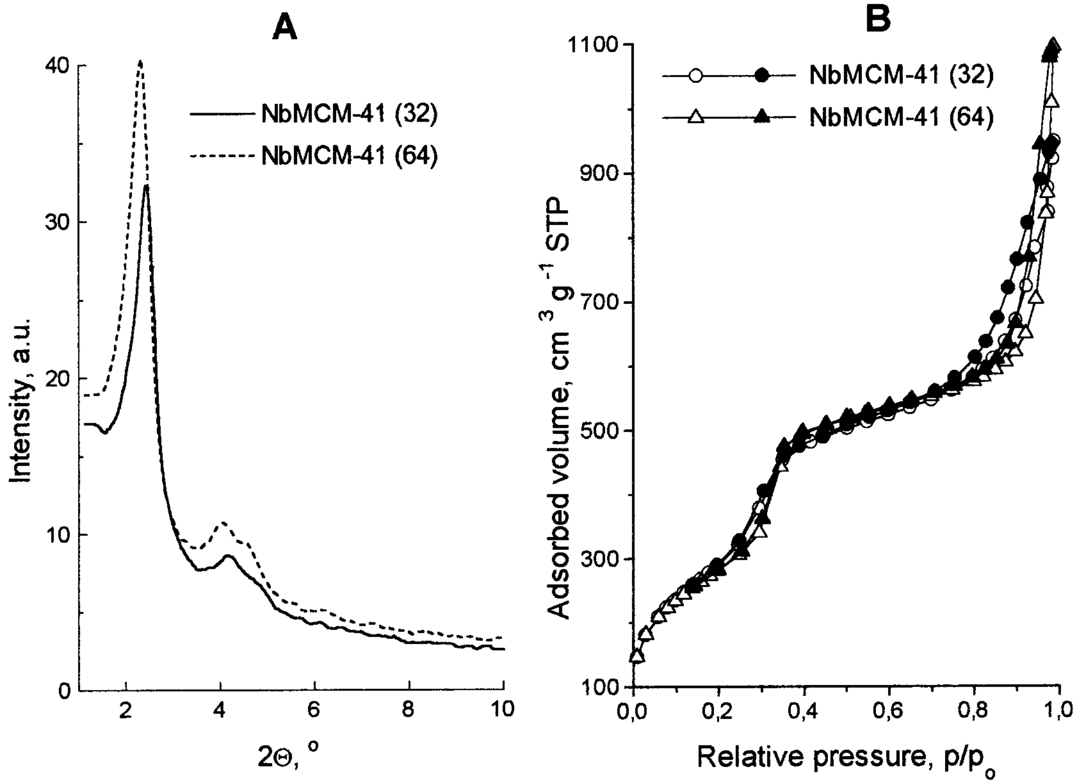


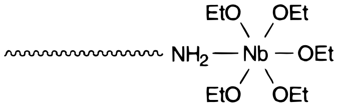
Figure 8. (A) XRD patterns of mesoporous materials of MCM-41 type containing niobium (number in parentheses indicates Si/Nb ratio). (B) N_2 adsorption (filled symbols)/desorption (open symbols) isotherms of niobium containing MCM-41 materials. (Reproduced with permission from ref 57. Copyright 1998 Nicolaus University Press.)

After heating the reaction mixture at 373 K for 24 h and then cooling it to room temperature, the pH was adjusted to 11 by the dropwise addition of oxalic acid with vigorous stirring. Following adjustment of the pH, the sample was heated for an additional 24 h. The resulting precipitated product was washed with distilled water, dried in air at ambient temperature, and calcined at 773 K. X-ray diffraction, N_2 sorption measurements (Figure 8), and transmission electron microscopy studies confirmed that the product exhibited the ordered mesoporous structure of NbMCM-41 when the initial Si/Nb ratio was 16, 32, and 64.[56,57] These synthesized materials exhibit cation exchange properties, which confirms the incorporation of niobium into the lattice of the NbMCM-41.[53,58] The niobium-containing MCM-41 structure is more mechanically stable than the related silica–alumina mesoporous molecular sieves. The hydrogen form of niobium-containing MCM-41 is less acidic than the analogous form of aluminum-containing MCM-41,[58] and this reduced acidity leads to a higher catalytic selectivity to thiols in the hydrosulfurization of alcohols.[59,60]

C. Mesoporous Oxides

The extension of MCM-41-like structures into the realm of pure transition metal oxides represents an important development from both the catalytic and electronic standpoints, because the variable oxidation states of transition metal oxides are useful in tailoring their catalytic, conductive, and magnetic properties.[61,62]

By taking advantage of the variable coordination chemistry that is possible at the metal center of an alkoxide such as tetraethyloorthosilicate or aluminum tri-*sec*-butoxide, Antonelli and Ying[63] recently succeeded in preparing a stable transition metal mesostructure from which the template could easily be removed. The authors first allowed niobium(V) ethoxide to react with a long-chain alkylamine in the absence of water to form an amino(tetraethoxy)niobium complex. In this way they obtained a covalent connection between two species as represented in



$$\sim\!\sim\!\sim\,\mathrm{NH_2{-}Nb(OEt)_4} \qquad (2)$$

Sufficient time was allowed for the complex to form ordered hexagonal structures, and then water was added to hydrolyze the Nb−O−C bonds. The condensation reaction started immediately and was reinforced by hydrothermal treatment. Template removal was most easily achieved by washing the sample with a HNO_3/EtOH solution at 313 K. In this way Nb-TMS-1, a mesoporous, hydrated niobium oxide, was obtained. This Nb-TMS-1 exhibited a specific surface area of 434 m^2 g^{-1}.[63]

In general, the synthesis of Nb-TMS-1 is strongly affected by the initial reaction conditions such as the temperature, the surfactant to metal ratio, the pH, and the nature of solvents:

(i) Aging up to 355 K increased the structural stability of Nb-TMS materials, probably due to the resulting increase in the material's crystallinity and an increase in its condensation, which leads to some degree of pore shrinkage.

(ii) Formation of Nb-TMS occurred at acidic or basic pH values. Amorphous niobia is formed at both the upper and lower ends of the pH scale.

(iii) Antonelli et al.[64] also studied the influence of headgroups on the synthesis of hexagonally packed niobium oxide. They concluded that sulfate, sulfonate, and hydroxyl surfactants yielded amorphous aerogels with high surface areas, broad pore size distributions, and no XRD patterns (after 1 h at 373 K); dimethylphosphino, methylamino, dimethylamino, 4-pyridino, and 2,4-pentanedionate surfactants (after 5 days at 373 K) also yielded materials with no crystalline patterns; carboxylate and 4-anilino surfactants gave materials that showed a broad amorphous hump centered at $2\Theta = 2°$ by XRD, and only the amino and phosphate headgroups produced discernible hexagonal phases. Amino surfactants generally are desirable over phosphate surfactants because the former are more easily removed.[64]

(iv) The materials that were obtained from the reactions having surfactant(dodecylamine) to Nb(OEt)$_5$ ratios of 0.3:1, 0.5:1, and 0.75:1 presented hexagonal arrangements of the pores (Nb-TMS1). The sharpness of the XRD peaks (100), (110), and (200) increased with an increase in the surfactant to alkoxide ratio. The sample prepared at a 1.5:1 surfactant to alkoxide ratio was a hexagonal phase (Nb-TMS2), which can be indexed to a *P63/mmc* unit cell.[64] A related mesostructured silica phase, SBA, prepared by Stucky[65] was also indexed in this space group. The materials prepared at ratios of 1.0:1 and 1.25:1 appeared to be either mixed phases or less crystallized single phases. At a 2.0:1 ratio, the material obtained was a layered MCM-50 analogue (Nb-TMS-4).

(v) Increasing the surfactant chain length favored the formation of layered and cubic phases. The sample prepared at an octadecylamine to Nb(OEt)$_5$ ratio of 0.75:1 was hexagonal (Nb-TMS-1). The sample prepared at a 1.0:1 ratio was cubic and can be indexed to a *Pm*3*n* space group (Nb-TMS-3), while that prepared at a 1.25:1 ratio was layered (Nb-TMS-4).[64]

Antonelli and Ying[63,64,66,67] proposed a new approach to the synthesis of transition metal oxide (particularly niobium oxide) mesoporous materials. In this synthesis, the surfactant headgroup is directly ligated to the metal alkoxide prior to hydrolysis and condensation. This permits the required interaction between the organic and inorganic phases before the introduction of water. Another key feature of this ligand-assisted templating (LAT) approach is that the metal was directly connected to the inorganic precursor without a charge-matching or hydrogen-bonding interaction.

Gimon-Kinsel and Balkus[68,69] reported a new method [called pulsed laser deposition (PLD)] to prepare Nb-TMS1. PLD has been proven to be an effective method for producing thin films, but the laser-deposited molecular sieve films generally have low crystallinity. Fortunately, the crystallinity of these films can be improved through reorganization induced by a brief hydrothermal treatment. The thin films of Nb-TMS1 have found applications such as capacitive-type chemical sensors and humidity sensors since Nb-TMS1 possesses semiconductor properties.

Other authors[70] also have explored the synthesis of channel structures within transition metal oxide frameworks. For example McCullen and Vartuli[71] prepared a stable salt−gel by reacting a surfactant niobotungstate salt with TEOS (tetraethylorthosilicate) to form a lamellar phase of MCM-50 type. During this treatment, Nb−O−Si linkages were formed. Removal of the cationic surfactant by acid extraction resulted in porous structures with surface areas up to 265 m^2 g^{-1}.

Recently, Abe et al.[72] prepared porous niobium oxide by the exfoliation of $K_4Nb_6O_{17}$. A composite of the niobate sheets and MgO particles was obtained by precipitating the exfoliated two-dimensional niobate sheets with MgO fine particles. Porous niobium oxide was formed after removal of the MgO particles from the composite via thermal treatment. The material prepared in this manner exhibited high photocatalytic activity.

A synthesis of the microporous niobium oxide molecular sieve Nb-TMS6 through the use of bifunctional templating molecules was performed by Sun and Ying.[73] Unlike Nb-TMS1 and Nb-TMS3, which displayed long-range packing of mesopores in hexagonal and cubic arrangements, respectively, the packing of micropores in Nb-TMS-6 appeared to be rather disordered with no clearly defined crystal phases.

Lately, porous niobia having three-dimensional structures patterned over multiple length scales were prepared by combining micromolding, polystyrene sphere templating, and cooperative assembly of inorganic sol−gel species with amphiphilic triblock copolymers.[74] A cubic mesophase resulted from the application of Pluronic F127 [$EO_{106}PO_{70}EO_{106}$−poly(ethyleneoxide)−b-poly(propyleneoxide)−b-poly(ethyleneoxide) with a general formula of EO_nPO_m-EO_n] as the structure-directing block copolymer species, whereas a hexagonal mesophase was obtained when Pluronic P123 ($EO_{20}PO_{70}EO_{20}$) was used.

VI. Other Niobium Compounds

Transition metal carbides and nitrides are well-known for their refractory, electronic, and magnetic properties. They have already found application in cutting tools, wear-resistant parts, and hard coatings and as electronic and magnetic components and superconductors. However, they have not yet been widely developed as catalysts.[75,76]

Nitrides are commonly prepared by direct interaction between transition metals and dinitrogen or ammonia. In the past decade, a new method of preparing nitrides has been developed using temperature-programmed nitridation of an oxide precursor, and this has led to materials with higher specific surface areas. Kim et al.[77] performed experiments with Nb_2O_5 and optimized the nitridation process. Niobium oxynitride with a face-centered cubic structure was prepared by a temperature-programmed synthesis method consisting of passing 20% (v/v) NH_3/He over Nb_2O_5 while heating to a final temperature in the range of 1027−1173 K.[78] A new family of bimetallic oxynitride compounds, M_I−M_{II}−O−N (M_I, M_{II} = Mo, W, V, Nb, Cr, Mn, and Co), has been synthesized by nitriding bimetallic oxide precursors with ammonia gas via a temperature-programmed reaction.[79] The temperature required for the synthesis is moderate (<1120 K), the cycles are short, and the parameters are easy to control.

Recently Zhou and Andrews[80] reported that laser-ablated niobium atoms reacted with nitrogen atoms and molecules during condensation with a pure nitrogen pass in an excess of argon. NbN and its dinitrogen complex were trapped, and NbN_2 was produced upon annealing in solid nitrogen. The same method was also applied to the preparation of NNbO, $Nb(\eta^1\text{-}NO)_x$ (where $x = 2, 3$) and $(N_2)(NbO_2)$ molecules in the reaction of laser-ablated niobium atoms with NO.[81]

A temperature-programmed method was also applied to the synthesis of niobium and bimetallic Nb−Mo carbides.[75,82,83] The carburization of β-niobium oxide (β-Nb_2O_5) to niobium carbide (NbC) in a 20% (v/v) CH_4/H_2 flow at temperatures above 1370 K takes place by the following steps:

$$\beta\text{-}Nb_2O_5 \xrightarrow[\text{fast}]{} NbO_2 \xrightarrow[\text{slow}]{} [NbO_xC_y] \xrightarrow[\text{fast}]{} NbC \qquad (3)$$

Niobium hydrides are formed by a chemical reaction between niobium metal powder (formed by ball-milling) and liquid decalin or tetralin when the reaction is carried out at room temperature and 1 atm.[84] Niobium carbide also is formed when metal powder is used in small quantities.

There is also evidence that silicon can form true interstitial compounds with group V metals (in contrast to the group VI−VIII elements). When Si is sputtered on Nb at temperatures of $900 < T < 1100$ K, the silicide $NbSi_2$ is formed. At temperatures of $1100 < T < 1200$ K, the silicide Nb_5Si_3 is formed, and at $T > 1200$ K, Nb_4Si is formed prior to the transformation of both silicides into $NbSi_2$. Sputtering Si at temperatures of $1200 < T < 1400$ K produces the silicide Nb_4Si.[85]

Niobium sulfide has received much attention in the past few years.[86] Like niobium oxide, it possesses unique acidic properties that are applicable to hydrotreating reactions. Unsupported niobium sulfides are usually prepared by direct combination of the elements in evacuated silica tubes followed by intercalation−deintercalation treatment to improve the surface area.[87] Niobium sulfides are very sensitive to support effects.[87] Usually carbon or alumina are used as their support.[86−88]

VII. Application in Heterogeneous Catalysis

A. Various Functions of Niobium Compounds in Catalysis

The function of niobium compounds in catalysis can be that of promoter or active phase, support, solid acid catalyst, or redox material.

1. Promoter or Active Phase

A supported metal oxide often shows a different catalytic activity from its bulk oxide. Therefore, many studies have been undertaken to determine the nature of supported niobium species. Thus, many investigations have attempted to control the surface species by selecting (i) suitable support materials (silica,[89−94] alumina,[95−98] magnesia,[95,98] titania,[95,96,99,100] zirconia,[95,96] and zeolites: Y-type[45−47] and ZSM-5[47,48,50]); (ii) niobium precursors (niobium chloride,[90,99] niobium oxalate,[95,97,98] niobium ethoxide,[89,95,97] niobium acid,[92,93,96,100] niobates,[101] and niobium complexes with hydrocarbon ligands[91,97]); and (iii) preparation methods (including the equilibrium adsorption of metal complexes in aqueous solution, which is a simple procedure for the preparation of uniform species dispersed on supports[93]).

Three different surface niobia species have been identified on oxide supports: 4-fold coordinated surface NbO_4 species that appear at very low surface coverages ($\theta_{Nb} \ll 1$), 5-fold coordinated surface NbO_5 species present at intermediate surface coverages ($\theta_{Nb} < 1$), and 6-fold coordinated surface NbO_6 found at high surface coverages ($0.5 < \theta_{Nb} < 1$). On silica, only NbO_4 is present because high surface coverages cannot be achieved on this support due to the low number and reactivity of the silica surface hydroxyls.[15]

The preparation method does not appear to influence the structure and the reactivity of the surface niobium oxide species on silica and is therefore not a critical parameter.[97] A series of Nb_2O_5/SiO_2

catalysts showed no dependence on the niobium source used, whether it was niobium oxalate in water, niobium ethoxide in propanol, or nonaqueous Nb allyl. These materials exhibited only surface NbO_4 species. Also the synthesis method did not affect the reactivity of the resulting materials, as each produced indistinguishable methanol oxidation results.

The formation and location of the surface niobium oxide species are controlled by the substrate's surface hydroxyl chemistry. The surface niobium oxide species are located in the outermost layer of the catalysts as an overlayer. Calcination temperature is an important parameter that controls the activation and deactivation of the supported niobium oxide catalysts, but it is not critical so long as moderate temperatures, 673−773 K, are used.[97] The identity of the specific oxide support is a critical parameter since it dramatically affects the reactivity of the surface niobium oxide species and determines whether its sites are active for redox or acid catalysis. Thus, the critical parameters that affect the catalytic properties of the supported niobium oxide catalysts are the specific type of oxide support used and the catalyst composition.[97]

Lewis acidity was found in all of the supported niobium oxide systems, while Brønsted acid sites were only detected in niobia supported on alumina and silica.[96] As previously discussed, basic support surfaces result in the formation of highly distorted NbO_6 groups whereas acidic surfaces lead to the formation of slightly distorted NbO_6, NbO_7, and NbO_8 groups.

The surface niobium oxide overlayer is quite stable even at high calcination temperatures due to the strength of the surface niobium oxide−support interaction (SOSI).[102] The other observed interactions are the metal−[non-SMSI oxide (SiO_2) promoted with SMSI oxides (e.g., Nb_2O_5)] interaction[103] and the strong metal−support (Nb_2O_5) interaction (SMSI),[89] in which Nb_2O_5 plays the role of a promoter or a support, respectively. Those interactions that allow the reactants to interact simultaneously with the metal and the promoter are the most relevant to catalysis. When the catalyst consists of metal particles covered by patches of promoter oxide, some steps in the overall reaction may be catalyzed at the metal−promoter−gas/liquid interphase. The creation of a metal−promoter perimeter has proven pivotal to the catalyst's performance in reactions such as ethane hydrogenolysis or CO hydrogenation. A supported metal−promoter interaction (SMPI) is observed in niobium oxide-promoted Rh/SiO_2 catalysts,[94,104,105] niobia-promoted Pt/Al_2O_3 catalysts,[106] and silica-supported $NiNb_2O_6$ catalysts.[107]

2. Support Effect

Niobium oxide has been used as an oxide support for such metals as Ru,[108] Rh,[109] Pt,[110−112] Re,[108] Ni,[113−115] Cr,[108,116] W,[108] Co,[117−119] V,[108,120,121] P,[120] Ge,[120] Mo,[108,120] Sb,[120] Pb,[120] Bi,[120] and Fe.[122] When used in this manner, the properties of the niobia are improved by the addition of these elements, while its high selectivity is still maintained.

Niobia is a typical SMSI oxide. The SMSI geometrically affects the catalysts' activities due to surface decoration. The catalytic activities observed in structure-sensitive reactions such as the hydrogenolysis of hydrocarbons are strongly suppressed by SMSI, but this suppression is moderate in structure-insensitive reactions such as the dehydrogenation of hydrocarbons.[123] However, very recently, Pârvulescu et al.[124] found that the activity-determining factor in hydrogenolysis reactions carried out on niobia-supported cobalt is not the SMSI but the effect of the crystallite size and/or the presence of toxins from the metal precursors, such as Cl^- from $NbCl_5$.

3. Solid Acid Catalyst

As was previously stated, niobic acid ($Nb_2O_5 \cdot nH_2O$) calcined at moderate temperatures of 373−573 K showed an acidic character ($H_o \leq -5.6$), although it became almost neutral when calcined at 873 K.[23] This suggests that niobic acid which contains water, i.e., Nb_2O_5 activated at relatively low temperatures, would be effective as a catalyst for reactions that liberate a water molecule. These reactions include esterification[125] or polycondensation,[126] which is usually carried out using solid acids. Niobium phosphate, which has a higher acid strength of $H_o \leq -8.2$, also shows remarkable activity in acid-catalyzed reactions in which water molecules participate. Niobic acid pretreated with phosphoric acid is another example of a solid acid catalyst with a high ratio of Lewis acidity/Brønsted acidity.[127]

The additivation of niobia with phosphate[128] led to the creation of strongly acidic sites on the surface of this oxide. The activity, selectivity, and stability exhibited by this catalyst in the cumene cracking reaction were similar to those of a zeolite-containing material, indicating that the active sites are Brønsted acids. In contrast, sulfate additivation of niobia[128] seemed to generate Lewis acid sites, as deduced from the poor stability of the material in the cracking reaction and the prominence of α-methylstyrene among its reaction products. The impregnation of phosphated niobia with nickel and tungsten appeared to poison the acidity of the support. Of course, mixed oxides containing niobia show different acidic properties.

Datka et al.[96] investigated the acidic properties of supported niobium oxide catalysts and found Lewis acidity in the silica-, magnesia-, titania-, and zirconia-supported systems, while Brønsted acid sites were only detected when the niobia was supported on alumina or silica. The number of Lewis acid sites (LAS) on the niobia/titania and niobia/zirconia catalysts decreased nonlinearly with niobia loading, which suggests that new LAS are formed in these systems as existing sites are occupied by the niobia. A linear decrease in the LAS concentration with an increase in niobia loading would mean that the LAS on the surface of the support disappear proportionally to the fraction of the surface occupied by the deposited niobia. The created Lewis acid sites are usually weaker than the LAS initially present on the oxide support. Brønsted acid sites appear when the niobium oxide species reaches a critical surface coverage (~0.5 monolayer) and then increase linearly as the surface coverage increases untill a maximum is reached at less than a monolayer.

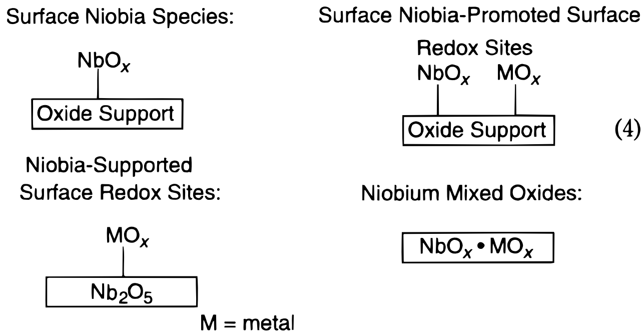
The addition of niobia to alumina is known to increase the surface acidity of the alumina, which increases its hydroprocessing activity.[129] Support compositions that maximize the surface acidity also maximize the removal of sulfur and nitrogen during hydroprocessing.

Moderate strength Lewis acid sites are generated during the dehydroxylation of hydrogen forms of Nb-containing mesoporous molecular sieves (H-NbMCM-41 materials).[58] Such materials can be useful catalysts for processes requiring the presence of Lewis acid sites where a high acid strength induces side reactions and/or coke formation. Thus, they have been proposed as catalysts for the synthesis of thiols and organic sulfides from alcohols and hydrogen sulfide.[56]

Although niobium-containing catalysts were studied in various acid-catalyzed reactions and their acidity was evaluated by various techniques, they have not been extensively used as acid catalysts in practice.

4. Redox Material

One of the major applications of niobium-based catalysts has been in the area of oxidation catalysis. Niobia catalysts may contain niobium oxide as a two-dimensional niobium oxide overlayer (surface niobia species), an oxide support (niobia-supported surface redox sites), or as mixed oxides (a solid solution or compound of niobium oxide) as shown:[130]



At low temperatures, surface niobia redox sites are only present on SiO_2, and the surface niobia species on other supports primarily act as acid sites. The addition of surface niobia species to vanadia/titania catalysts does not change the molecular structure or redox properties of the surface vanadia species. However, the surface niobia species may or may not influence the catalysts' activities. Specifically (i) reactions requiring only one surface vanadia redox site are not influenced by the surface niobia species (e.g., methanol oxidation) and (ii) reactions requiring adjacent surface redox and acid sites are enhanced by the surface niobia species (e.g., the SCR reaction). The redox potential of niobia enhances the redox properties of some metal oxide species (V, Cr, Mo, etc.) supported on Nb_2O_5. The introduction of niobia to mixed oxide catalysts can result in enhanced activity and selectivity (as for example in Bi−Nb−O, Nb−Ta systems).[130,131]

Wachs et al.[130,132] found that only the surface niobia species on silica give rise to methanol oxidation products (primarily formaldehyde and methylformate) while the surface niobia species on alumina, titania, and zirconia primarily lead to the formation of acidic products (dimethyl ether). Thus, the nature of the oxide support controls the redox properties of the surface niobia species.

A metal oxide (i.e.v, V_2O_5) species can be deposited over a large surface area of a niobia support by reaction of the surface hydroxyls of niobia with vanadium triisopropoxide oxide. A comparison of the reactivities of surface vanadia species loaded on various oxide supports in the methanol oxidation reaction reveals that niobia-supported vanadia species are among the most active catalytic systems for this reaction.[132] This high reactivity is associated with facile reduction of the bridging V−O−Nb bond and reflects the favorable redox potential of the niobia support as compared to less reducible supports such as silica and alumina. The redox potential of the niobia support also enhances the redox properties of other reducible surface metal oxide species (V, Cr, Mo, and Re).[130]

The incorporation of niobium (together with silicon) into the lattice of mesoporous molecular sieves of MCM-41 type generates materials with high oxidation properties as evidenced by their very high activity in the oxidation of thioether using hydrogen peroxide.[133] The oxidizing properties of the NbMCM-41 materials are due to the presence of an active lattice oxygen, which is formed during the dehydroxylation of the molecular sieves and can be identified by ESR measurements. The generation of this active oxygen is accompanied by the formation of Lewis acid sites as established by FTIR studies following pyridine and lutidine adsorption.[58]

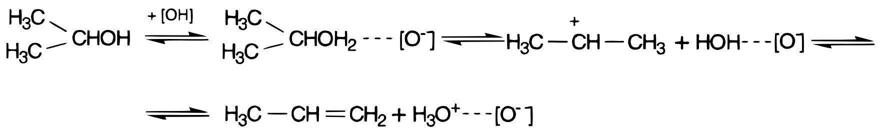
When niobium oxide is reduced appropriately, it becomes active in the catalytic isomerization and oligomerization of olefins. This activity is very sensitive to the conditions under which the niobium oxide reduction was carried out and depends on the isolation of a Nb^{4+} cation from another Nb^{4+} center.[134]

B. Catalytic Activity of Materials Containing Niobium

Niobium compounds and materials are becoming important as catalysts for various reactions, and interest in them is growing. Various types of reactions in which niobium catalysts were studied are described below:

1. Dehydration of Alcohols

Alcohols can be dehydrated either intramolecularly to olefins (eq 5) or intermolecularly to ethers (eq 6). Both processes require the presence of Brønsted acid sites on the catalyst surface. These acid centers participate in the proton transfer, as shown below in the 2-propanol dehydration example:



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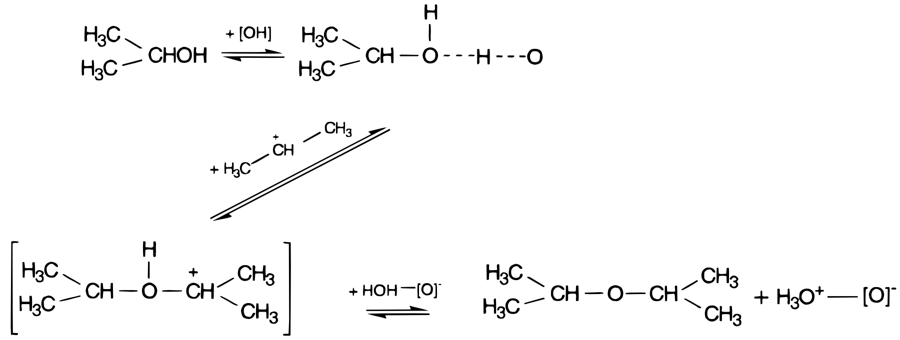


(6)

Niobium(V) oxide that has been treated at 373 K is characterized as a very strong Brønsted acid and can be used as a catalyst for Brønsted acid-catalyzed reactions under mild conditions. In fact, niobium oxide exhibits the highest acid strength of all the metal oxides pretreated at 373 K.[23] Thus, niobic acid appears to be the most suitable solid acid catalyst for dehydration, since its acidity not only does not decrease but may even increase in some cases upon contact with water vapor.[2] Many authors have reported high activities for niobium oxide in the dehydration of 2-propanol,[135] 2-butanol,[23] cyclopentanol, and cyclohexanol.[2] Crystallized niobic acid calcined at 573 K was found to show higher activity in the dehydration of 2-propanol than uncrystallized niobic acid, niobic acid washed with water, or niobic acid treated with sulfuric or phosphoric acid.[18] However, it is well-known that treatment at higher temperatures (823 K) causes niobic acid to decompose to a crystalline niobium oxide whereupon it loses its acidic properties and catalytic activity. Both its acidity and activity can be remarkably enhanced by treatment with sulfuric or phosphoric acid though. For example, the surface acidity and the catalytic activity of H_3PO_4-treated niobic acid are well maintained at temperatures as high as nearly 873 K.[34]

Niobic acid treated with phosphoric acid is not only active in the intramolecular dehydration of alcohols but also promotes intermolecular dehydration reactions such as the conversion of methanol to dimethyl ether (DME).[35] This catalyst is also effective in the synthesis of methyl *tert*-butyl ether (MTBE) from *tert*-butyl alcohol (TBA) and methanol, but the TBA conversion and the selectivity to MTBE are not significantly improved over those obtained using amorphous niobium phosphate, $NbOPO_4$.[36] Niobic acid treated with phosphoric acid does produce higher yields of MTB than other metal oxides such as TiO_2, ZrO_2, Al_2O_3, SiO_2, and SiO_2-TiO_2 (Table 4).

The rate constants for the intra- and intermolecular dehydration of alcohols can be controlled by altering the Nb structures. For example, Nb dimers on SiO_2 are active and selective for the dehydration of ethanol and produce the smallest amount of ethene via intramolecular dehydration.[90,135]

Table 4. Catalytic Activities for the MTBE Synthesis of Niobium Phosphate and the Other Solid Acids[a]

catalyst	TBA conversion (mol %)	MTBE selectivity (mol %)
niobium phosphate	82.2	35.5
H_3PO_4-treated Nb_2O_5	77.2	33.6
$Nb_2O_5 \cdot H_2O$	0.8	17.5
H_3PO_4-treated TiO_2	30.6	37.6
TiO_2	0	0
H_3PO_4-treated ZrO_2	12.0	32.4
ZrO_2	0	0
H_3PO_4-treated Al_2O_3	1.7	8.1
Al_2O_3	0	0
H_3PO_4-treated SiO_2	99.2	7.2
SiO_2	0	0
solid H_3PO_4	99.4	5.5
H_3PO_4-treated SiO_2-TiO_2	99.3	6.1

[a] Reproduced from ref 35. Copyright 1993 Elsevier Science.

Ethanol decomposition is also observed on nickel ion-exchanged layered potassium niobate, $Ni-K_4Nb_6O_{17}$, and occurs more rapidly than on Nb_2O_5. The formation of diethyl ether from ethanol predominates on bulk niobium oxide but is not observed on $Ni-K_4Nb_6O_{17}$. The $Ni-K_4Nb_6O_{17}$ has a layered structure consisting of niobium oxide sheets with potassium ions located between the different interlayers. *n*-Propanol also decomposes with a higher conversion on $Ni-K_4Nb_6O_{17}$ than on Nb_2O_5 and shows no formation of dipropyl ether.[136]

A pillared lanthanum−niobium oxide of perovskite type, $ALaNb_2O_7$, when combined with TiO_2 or ZrO_2, exhibits high activity for the dehydration of methanol to DME and of 1-butanol to 1-, *cis*-2-, and *trans*-2-butenes.[137]

Recently, a new type of solid acid material, a silica pillared lanthanum niobate with a supergallery of 1.74 nm, was investigated using the decomposition of 2-propanol at 573 K as a probe reaction.[138] This material showed complete conversion of the reactant to dehydration products indicating a catalytic activity comparable to that of niobic acid. However, the authors did not report the selectivity among the various products that might have helped in the characterization of the catalyst.

2. Dehydrogenation

The dehydrogenation of long chain paraffins (according to the reaction $C_nH_{2n+2} \rightarrow C_nH_{2n} + H_2 \rightarrow C_nH_{2n-2} + 2H_2$) is usually performed using alumina-supported bimetallic catalysts. *n*-Heptane dehydrogenation on Pt/Nb_2O_5 displayed a higher selectivity for the formation of olefins than did conventional catalysts.[112,139,140] Also the formation of aromatics and light products was minimized. The selectivity increased with the platinum content. The same trend was observed for the dehydrogenation of cyclohexane.

Nickel niobate ($NiNb_2O_6$) supported on SiO_2 showed a TOF (turnover frequency) in the dehydrogenation of cyclohexane to benzene[101] similar to that of Pt/Nb_2O_5 at the highest platinum loading but produced a higher selectivity for benzene (~100%). These results demonstrate that selectivity is improved by the Ni–Nb interaction.

3. Oxidative Dehydrogenation

The oxidative dehydrogenation (ODH) of alkanes offers an energetically attractive route to the production of alkenes (i.e., $R{-}CH_2{-}CH_3 + O_2 \rightarrow R{-}CH{=}CH_2 + H_2O$). Since ethane is the second most major component of natural gas and is also a main product in many methane-coupling reactions, its transformation to ethene at low temperature is of considerable interest. The metal oxide catalyst containing Mo, V, and Nb ($Mo_{16}V_4Nb_2$) is more active (10% of conversion at 559 K) and selective (100%) than other mixed-metal oxides (Mo–V, Mo–Mn, Mo–Ti, etc.).[2] Burch and Swarnaka[141] found that a molybdenum–vanadium–niobium oxide (Mo:V:Nb = 6:3:1) is highly selective for the oxidative dehydrogenation of ethane to ethene. The presence of all three oxides is necessary in order to have an active and selective catalyst. The best results, according to Somorjai et al.,[142] have been obtained using a mixture with a Mo–V–Nb ratio of 19:5:1. Their studies suggest that the active phase is based on molybdenum and vanadium. Niobium enhances the intrinsic activity of this combination and improves the reaction selectivity by inhibiting the total oxidation of ethane to carbon dioxide.

The oxidative dehydrogenation of propane may provide an attractive route to the production of propylene and could be a good alternative to conventional dehydrogenation and cracking processes. Various Nb-containing catalysts were studied for the oxidative dehydrogenation of propane. Smits et al.[143] found that niobium oxide shows a very high selectivity in this reaction although the conversion was very low (Figure 9). The activity of the niobia was improved without diminishing its selectivity by adding other suitable elements (V, Cr, Mo).[2] Smits et al.[120] found that vanadium and chromium, which occupy unique environments make these catalysts selective for propylene. The influence of various preparation methods on the performance of the V–Nb–O catalysts also was investigated by Smits et al.[144,145] They found that the activity and selectivity of a given vanadium site depends on the nature of its neighboring atoms. Vanadium neighbors promote the activity, while niobium neighbors promote the selectivity. Niobium is much more difficult to reduce than vanadium and this feature improves the selectivity, since facile reduction often causes low selectivity in these reactions. Watling et al.[121] examined Nb_2O_5 supported monolayer V_2O_5 catalysts and vanadia–niobia catalysts with different vanadium oxide loadings and concluded that all the samples show similar TOFs when the rates are normalized for the concentration of V on the surface. The reaction's propene selectivity strongly depends on the nature of the catalysts used because propene's re-adsorption and interaction with the acidic sites leads to total oxidation.

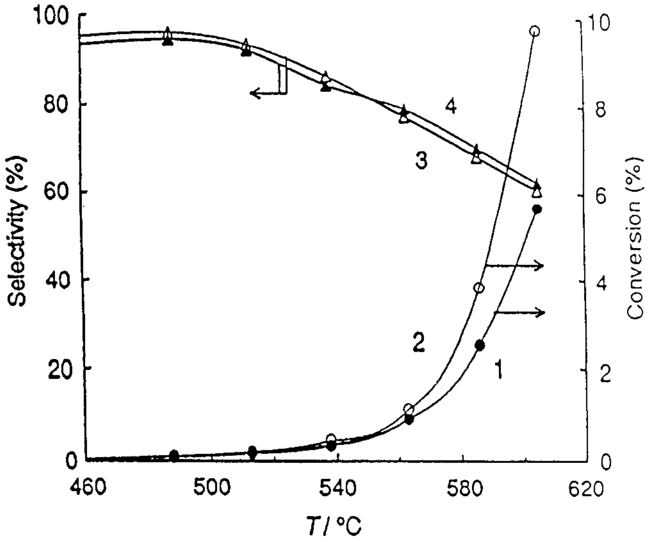
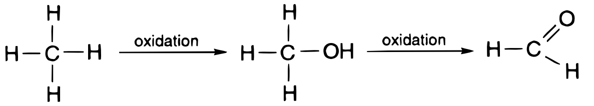


Figure 9. Propane conversion and propene selectivity on Nb_2O_5 calcined at 1125 K. Lines 1 and 3 are for 5% O_2; lines 2 and 4 are for 10% O_2. (Reproduced with permission from ref 143. Copyright 1991 The Royal Society of Chemistry.)

When butane is used as the reactant, the process occurs more readily than when propane and ethane are used. A $Nb_2O_5{-}Cr_2O_3/ZrO_2$ catalyst was reported to be active in the formation of 1-butene (0.12 mol fraction), *cis*-2-butene (0.16), *trans*-2-butene (0.234), and isobutene (0.48) from butane at 723 K.[2]

4. Oxidation and Ammoxidation

In recent years much research has focused on the direct partial oxidation of methane to oxygenates (i.e., methanol and formaldehyde), especially methanol, according to



$$\mathrm{H{-}\underset{H}{\overset{H}{C}}{-}H} \xrightarrow{\text{oxidation}} \mathrm{H{-}\underset{H}{\overset{H}{C}}{-}OH} \xrightarrow{\text{oxidation}} \mathrm{H{-}C({=}O){-}H} \qquad (7)$$

Dimethyl ether is also formed as a result of the intermolecular dehydration of methanol.

The direct conversion of methane to methanol has proven to be an extremely demanding reaction, due to the harsh conditions required to activate the methane molecule and the thermodynamic instability of the desired products with respect to the combustion product CO_2. Several oxides such as MoO_3, Nb_2O_5, Ta_2O_5, and WO_3 have been shown to catalyze this reaction. Methanol conversion over these materials was high, and the major products were formaldehyde and dimethyl ether.[146] A high selectivity toward CH_3OCH_3 was induced by surface niobium oxide monolayers on TiO_2, ZrO_2, and Al_2O_3,[23,97] or 1%

Table 5. Catalytic Properties of Methanol Oxidation Reaction over Surface-Modified Niobium Oxide Catalysts at 503 K (All Samples Were Calcined)[a]

catalysts	activity (mmol g^{-1} h^{-1})	selectivity (%) HCHO	CH_3OCH_3	$(CH_3O)_2CH_2$	$CO + CO_2$
Nb_2O_5	5.8	5	95		
1% P_2O_5/Nb_2O_5	36.2		100		
1% SO_4^{2-}/Nb_2O_5	32.0		100		
1% CrO_3/Nb_2O_5	41.0	45.3	46.9	4.5	1.0
1% WO_3/Nb_2O_5	10.7		98.3		1.7
1% Re_2O_7/Nb_2O_5	8.0	30.4	58.3	5.5	5.8
1% MoO_3/Nb_2O_5	15.0	21.8	69.2	7.5	1.5
1% V_2O_5/Nb_2O_5	74.2	61.4	35.2		3.4

[a] Reproduced from ref 108. Copyright 1992 Elsevier Science.

CrO_3 supported on Nb_2O_5, which possesses the acidity required for the dehydration of methanol to ether.[116]

The influence of the surface metal oxide and acid species of surface-modified niobium oxide catalysts with low loading (1 wt %) on the catalytic activity and selectivity obtained during methanol oxidation was studied by Jehng et al.[108] (Table 5). The niobia's surface phosphate and sulfate species increase the methanol conversion and induce 100% selectivity to the dehydration product CH_3OCH_3. The WO_3/Nb_2O_5 system was somewhat less active in this reaction than the other metal oxide systems examined. Surface chromium, rhenium, vanadium, and molybdenum oxide species, which enhance the reduction sites on niobia, produced higher selectivities to HCHO, with the V_2O_5/Nb_2O_5 system exhibiting the highest activity among these catalysts.

Redox products (mainly methyl formate and formaldehyde) are obtained when silica-supported niobium oxide is used to catalyze the methanol oxidation reaction. Jehng et al.[147] found that surface niobium oxide species were partially reduced by reaction environment.

The oxidation of higher hydrocarbons were also studied using various catalysts. Ethane was converted to acetic acid with a 63% selectivity and to ethylene with a 14% selectivity in the presence of oxygen at 528 K through the use of a $Mo_{0.7}V_{0.25}Nb_{0.02}Sb_{0.61}Ca_{0.01}O_n$ catalyst, although the conversion was low (3%).[2] The same reaction was studied by Ruth et al.[148] using Mo(73)V(18)Nb(9)O(x) as the catalyst. They found that all phases of the catalyst catalyzed the oxidative dehydrogenation of ethane to ethene, while only the $Mo_6V_9O_{40}$ phase lead to the formation of acetic acid. Unfortunately, vanadium oxide supported on niobia showed very low activity in the selective oxidation of ethane despite its acidity.[149]

The oxidation of butane to maleic anhydride is known to be catalyzed by $(VO)_2P_2O_7$. The reaction proceeds via the dehydrogenation of butane to butene followed by oxidation of butene: i.e., $C_4H_{10} \rightarrow C_4H_6 \rightarrow C_4H_4O \rightarrow C_4H_2O_3$ (MA, maleic anhydride). Wachs et al.[150] studied this butane oxidation over a titania-supported vanadium oxide catalyst. The butane and maleic acid TOFs increased by a factor of 4 when an acidic niobium oxide was introduced to the 1% V_2O_5/TiO_2 catalyst. The niobia species coordinate to the surface of the titania support and only interact with surface vanadia species via lateral interactions in the monolayer. Thus, it is the presence of these acidic niobium oxide sites adjacent to the surface vanadia that has a beneficial effect on the butane oxidation TOF and on the maleic anhydride selectivity. Mastuura and co-workers[42] found that the VNbPO catalyst exhibits high catalytic activity in the oxidation of butane and butene to maleic anhydride. At a reaction temperature of 673 K, $(VO)_2P_2O_7$ produced an 88% conversion of butene and a 53% selectivity to MA, while a VNbPO catalyst with a Nb/Nb + V ratio of 0.05 yielded an 88% conversion of butene and a 56% selectivity to MA.

Ammoxidation is an important process. Acrylonitrile ($H_2C{=}CH{-}CN$, ACN) is an intermediate used in the preparation of fibers, synthetic resins, synthetic rubbers, etc. Presently, ACN is produced by the ammoxidation of propene in a fluidized-bed reactor using a mixed metal oxide catalyst. V−Sb, Bi−Mo, P−V, VPO, or Fe−Sb mixed oxides, which are commonly used as catalysts, require temperatures of 773 K or higher and give yields of ACN that do not exceed 40%. A new catalyst, a Mo−V−Nb−Te mixed metal oxide reported by Ushikubo et al.[151] is highly active and selective for this reaction. The efficiency of this catalyst is higher than those of the V−Sb and Bi−Mo mixed oxide catalysts, and it produces higher yields of ACN at a lower temperature. The feed composition was optimized for this Mo−V−Nb−Te mixed oxide catalyst by Vaarkamp and Ushikubo.[152] The optimal feed consisted of propane, ammonia, and oxygen in a ratio of 1:1.2:3.

The ammoxidation of ethane to acetonitrile is catalyzed fairly well by $Nb_2O_5{-}Sb_2O_5/Al_2O_3$ with an atomic ratio of Nb/Sb = 5:1.[153] Likewise, the ammoxidation of ethane proceeds with a conversion of about 40% and a selectivity to acetonitrile of 78% in the presence of a $Mo_{1.0}V_{0.4}Te_{0.2}Nb_{0.1}O_n$ catalyst.[2] The ammoxidation of isobutane to methacrylonitrile is catalyzed by the well-known ammoxidation catalyst, $Bi_2Mo_3O_{12}$, but with only about a 4% conversion and about a 60% selectivity to methacrylonitrile and methacrolein at 733 K. However, the addition of a niobium compound to this bismuth molybdate, with or without the addition of Fe or Co, increases both the conversion and the selectivity obtained from the reaction.[154]

5. Oxidative Coupling of Methane

The addition of niobium oxide to the catalyst enhanced the oxidative coupling of methane (OCM) to C_2 species (ethane and ethene) such that Li/MgO

Table 6. Catalytic Activity of Amorphous Niobium Phosphate for Various Esterifications with Acetic Acid at 493 K[a]

alcohol	conversion to ester (mol %) liquid phase	conversion to ester (mol %) vapor phase
n-C_4H_9OH	91.5	92.6
iso-C_4H_9OH	83.6	70.2
s-C_4H_9OH	82.9	1.0
t-C_4H_9OH	9.7	0
C_2H_5OH	80.4	
CF_3CH_2OH	14.4	
$CH_2{=}CHCH_2OH$	82.3	

[a] Reproduced from ref 35. Copyright 1993 Elsevier Science.

promoted by niobium oxide showed a higher activity than pure Li/MgO in the temperature range in which the reaction was studied (ca. 923−1003 K).[155]

The OCM of methane to higher hydrocarbons also was investigated using two types of semiconductor catalysts, NbO (p-type) and Nb_2O_5 (n-type), at 1 atm pressure.[156] The results indicated a strong correlation between C_{2+} selectivity and the electronic properties of the catalyst in terms of p- vs n-type conductivity. The p-type semiconductor catalyst exhibited a higher selectivity (95.92%) than the n-type catalyst (23.08%) at a methane conversion of 0.64%. However, the beneficial effect of p-type conductivity in an OCM catalyst has been emphasized by only a few researchers (i.e., Dubois and Cameron,[157] Norby and Anderson[158]). The NbO and Nb_2O_5 catalysts differ in other parameters besides conductivity, and these other parameters also can affect the selectivity of the catalysts.

6. Esterification

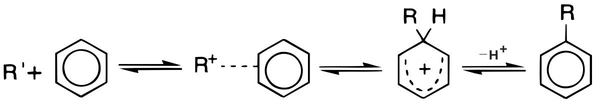
The reaction of alcohols with carboxylic acids to form esters may be performed in either a liquid or a vapor phase in the presence of various acidic or basic catalysts. Among the various solid acid catalysts, niobic acid seems to be the most suitable for esterification reactions, because when hydrated it has a fairly high acid strength and is resistant toward water vapor. According to Chen et al.,[125] the esterification of acetic acid with ethanol proceeded at 393 K in the presence of niobic acid heat-treated at 473 K with a 100% selectivity to ester and a 72% conversion. No catalyst deactivation was observed after 60 h of use. The conversion obtained was higher than those of the cation exchanged resin, $SiO_2{-}Al_2O_3$, and H-ZSM-5.

Niobic acid likewise promoted the esterification of acrylic acid with methanol to form methyl methacrylate (MMA). In this reaction, both a high conversion (95.1%) of acrylic acid and a high yield (95%) of MMA were obtained by decreasing the space velocity and increasing the MeOH/acid molar ratio.[159]

The catalytic activity of niobic acid is somewhat increased by treating it with sulfuric acid.[18] Furthermore, niobium phosphate showed a fairly high conversion (91.5, 83.6, and 52.9%) in the liquid-phase esterifications of n-butyl, isobutyl, and s-butyl alcohol, respectively, with acetic acid at 493 K.[36] It is interesting to note that the catalysts that esterified s-butyl alcohol in the liquid phase did not promote the vapor phase estrification well (Table 6). The liquid-phase esterification of acetic acid with 1-decanol, a long chain alcohol, was catalyzed more effectively by niobic acid than by other strong acids such as $SiO_2{-}TiO_2$ and $SiO_2{-}Al_2O_3$.[36]

7. Alkylation

The catalysis of organic reactions by inorganic solids is an important new area in preparative organic chemistry. The alkylation of aromatics is an important process in both the petroleum and the chemical industries. Alkylation occurs as the result of a carbenium ion formed from the alkylation agent interacting with the π electrons in the aromatic ring according to



(8)

Some alkylation reactions in which Nb-containing catalysts were studied are described below. Recently, it was found that niobic acid is active as a catalyst for the alkylation of benzene with methanol and that the catalytic activity is markedly enhanced when the catalyst is treated with a dilute phosphoric acid solution.[2] As shown in Table 7, amorphous niobium phosphate promoted the alkylation of benzene with olefins and alcohols. In particular, the phosphate promoted cumene synthesis via the alkylation of benzene with propene.[36] Higher conversions of propene (>95%) and benzene (>15%) and a higher selectivity (91%) to cumene were obtained at higher reaction temperatures (>558 K) when the alkylation of benzene with propene was carried out in the liquid phase.

Niobic acid pretreated with phosphoric acid at 423 K gave a very high conversion of benzyl alcohol (99.2%) during the benzylation of anisole. The same catalyst also was active in the benzylation of toluene, but the conversion of the alcohol was lower.[127]

Table 7. Alkylation of Benzene with Various Alcohols and Olefins over Amorphous Niobium Phosphate[a]

alkylation reagent	molar ratio of alkylation reagent vs benzene	reaction temp (K)	benzene conv. after 1 h (mol %)	selectivity of monoalkylated product (mol %)
$(CH_3)_2CHOH$	2.3	623	9.1	82
C_2H_5OH	1.5	673	3.1	77
CH_3OH	2.2	673	5.5	47
$CH_3CH{=}CH_2$	2.0	623	17.3	42
$(CH_3)_2CH{=}CH_2$	2.0	623	3.7	30
$CH_2{=}CH_2$	1.5	673	1.5	27

[a] Reproduced from ref 35. Copyright 1993 Elsevier Science.

Gilbert et al.[160] reported that the vapor-phase alkylation of phenols with methanol proceeds catalytically when carried out on niobium phosphate. The O-alkylation selectivity observed in this reaction decreases with an increase in the reaction temperature. Other alkylations, such as the alkylation of biphenyl with propene or isopropyl alcohol were also studied.[2]

8. Isomerization

The isomerization of olefins can be referred to cis−trans, skeletal, or double bond isomerization. Carbenium ion formation plays an important role in this process and requires a Brønsted acid catalyst. The butene and dimethyl butene isomerization activities of Nb-containing materials are described below.

$Nb_2O_5 \cdot nH_2O$, which was evacuated at 373 K for 2 h, showed remarkable 1-butene isomerization activity with a selectivity (*cis*-2-butene/*trans*-2-butene) of less than unity. The activity decreased drastically after the sample was evacuated at 573 K but was almost completely restored upon the introduction of water vapor followed by evacuation at 373 K.[23]

It is well-known that low ratios of *cis/trans*-2-butene obtained from the isomerization of 1-butene indicate an acidic catalyst. Therefore, this reaction is often used as a test to monitor the acidity of samples such as niobia aerogels prepared at supercritical drying temperatures.[16,20] Hasegawa et al.[161] concluded that Nb_2O_5 and Nb_2O_5/Al_2O_3 both exhibit an induction period prior to the isomerization of 1-butene. The highest activity in this reaction was observed using Nb_2O_5 (10 wt %) on Al_2O_3 (68%) as the catalyst.

Similar selectivities were obtained for 3,3-dimethyl-1-butene isomerization using niobium oxide or phosphate, or a USHY zeolite as the catalyst.[36] Each of these catalysts underwent a rapid initial deactivation followed by a slower decrease in their activity.

9. Hydrogenolysis

Ethane hydrogenolysis (which is usually catalyzed by group VIII metals) is a typical structure-sensitive reaction, and large ensemble sites are required for high catalyst activity. Therefore, it is interesting to note that $RhNbO_4$ particles exhibit high activity in this process.[103] The hydrogenolysis of propane over supported nickel catalysts (Ni/Nb_2O_5)[162] and the hydrogenolysis of 2-methylbutane and *n*-pentane over Pt/Nb_2O_5 or Rh/Nb_2O_5 have also been reported.[110]

10. Disproportionation of Hydrocarbons (Methathesis)

The disproportionation of some hydrocarbons has been studied using catalysts that contain niobium oxides either as a support or as a promoter. Methyltrioxorhenium (CH_3ReO_3) supported on $Nb_2O_5 \cdot H_2O$ showed pronounced catalytic activity in the methathesis of *cis*-2-pentene and 1-pentene. Maximum activity was obtained when the $Nb_2O_5 \cdot H_2O$ was evacuated at 473−573 K prior to the addition of CH_3ReO_3.[163]

Very promising heterogeneous methathesis catalysts have been developed by anchoring aryloxy tungsten complexes on a NbO_x/SiO_2 support. The catalytic activity of the $WCl_4(OC_6H_3X_2\text{-}2,6)_2/NbO_x/SiO_2$ ($X = Br$ or Bu^t) precursors activated by Bu^iAlCl_2 was very high in pent-2-ene (cis + trans) methathesis.[164]

The addition of Nb_2O_5 as a promoter to Re_2O_7/Al_2O_3 led to high catalyst activity for 1-hexene methathesis. At higher niobia loadings, however, the catalytic activity quickly decreased.[165]

11. Hydrogenation

In Fischer−Tropsch synthesis, which is the hydrogenation of CO with H_2 to form hydrocarbons, the activity and selectivity of the metal catalyst are highly sensitive to the nature of its support oxide. When Rh is the catalyst, the support effect decreases in the order $Nb_2O_5 > ZrO_2 > Al_2O_3 > SiO_2 > MgO$.[166] At 493 K, the conversion of CO on Rh/Nb_2O_5 was almost 76% in contrast to the negligible conversion (1.4%) obtained over Rh/Al_2O_3[167] and also higher than on Rh/SiO_2.[123] In addition to CH_4, C_2-C_5 hydrocarbons were obtained when using the Rh/Al_2O_3 catalyst.

A Ni/Nb_2O_5 catalyst was also reported to show a much higher conversion than Ni/Al_2O_3[2] or Ni/SiO_2 in the Fischer−Tropsch reaction.[167] Fe/Nb_2O_5 exhibited a very high conversion and a very good selectivity toward higher hydrocarbons.[122] Reducing a Co/Nb_2O_5 catalyst resulted in improved selectivity toward C_5^+ compounds combined with a low selectivity toward C_1 at 533 K.[117] Niobia-supported cobalt catalysts prepared by other authors[118] showed very high selectivities toward linear hydrocarbons in the diesel range ($C_{13}-C_{18}$). The addition of Rh in various amounts to Co/Nb_2O_5 increased its C_5^+ hydrocarbon selectivity and promoted the formation of oxygenated compounds.[119]

The short summary presented above clearly indicates the importance of Nb_2O_5 as a support for various metals that are active in the Fischer−Tropsch synthesis. The choice of metals used in the catalyst controls the formation of the desired hydrocarbons.

12. NO Reduction

The selective catalytic reduction (SCR) of NO_x by ammonia has been extensively employed in industry over the past few years for controlling pollution due to nitrous gases. In general, it is accepted that the SCR of nitric oxide is based on the following reaction:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \qquad (9)$$

Mixed oxides of TiO_2, especially V_2O_5/TiO_2, have often been used as catalysts, since the reaction requires the presence of both redox and acidic centers on the catalytic surface. Niobium oxide exhibits a fairly high catalytic activity for NO removal when it is supported on or mixed with TiO_2.[2] The maximum conversion (97%) of NO on $V_2O_5-Nb_2O_5/TiO_2$ was observed at 543−553 K, while V_2O_5/TiO_2 required higher temperatures (573−583 K) to reach this same level of conversion.[99]

The presence of surface niobia species on titania had a dramatic effect on the catalytic activity and selectivity obtained in the SCR process. The activity at low temperatures increased by approximately an order of magnitude, and the selectivity toward N_2 formation at complete conversion of NO was essentially 100%. Although the addition of tungsten oxide (the conventional promoter) to the surface of the titania-supported vanadia catalyst also increased the activity, the presence of the surface tungsten oxide species resulted in a somewhat lower selectivity toward N_2 formation at 100% conversion of NO.[130] Wachs et al.[168] concluded from their SCR work carried out using vanadia catalysts supported on TiO_2, Al_2O_3, and SiO_2 that the reaction proceeds via a dual-site mechanism, involving a surface vanadia redox site and an adjacent surface nonreducible metal oxide site. Such dual sites are generated as the surface coverage of vanadia species increases or through the addition of a promoter such as niobium. Generating dual sites on the surface results in a 5−10-fold increase in the SCR TOF. The selectivity to N_2 in this system depends on the specific oxide support ($TiO_2 > Al_2O_3 > SiO_2$), the temperature (selectivity decreases at higher temperature due to the oxidation of NH_3 and NO to N_2O), and the surface concentration of redox sites (selectivity decreases as the concentration of pairs of surface redox sites increases, since these lead to N_2O formation).

Sazonova et al.[169] developed a procedure for preparing V−Ti oxide SCR catalysts based on local raw materials. Following the addition of tungsten or niobium oxides, these catalysts were studied in sulfur dioxide oxidation and in the selective catalytic reduction of NO by ammonia. Niobium-free catalysts used in the oxidation of SO_2 to SO_3 showed a considerable decrease in their SCR activity at temperatures below 623 K. Thus, when added to V−Ti oxide catalysts, niobium oxide suppresses sulfur dioxide oxidation and increases the catalyst's activity in the SCR process. The same behavior was also observed when tungsten was added to the catalysts.

Furthermore, it is noteworthy that the addition of Nb_2O_5 to the most commonly used metal oxide, FeO_x, is effective for improving the catalyst's behavior. A small amount (5 at %) of Nb_2O_5 added to FeO_x causes a remarkable enhancement of the SCR activity, such that the conversion reaches 90% at 573 K.[1]

The catalytic reduction of NO by CO to form CO_2 and N_2O proceeds at quite a low temperature (300 K) over platinum supported on TiO_2 and Nb_2O_5. The absence of water suppresses N_2 formation. The effect of water was most pronounced on the n-type semiconductor form of Nb_2O_5.[111]

In the past decade there has been much interest in niobium catalysts (as evidenced by the many new patents on their processes) for the removal of nitrogen oxides, as three-way catalyst materials,[170] and as catalysts for (i) decompositions,[171] (ii) the reduction of nitrogen oxides with hydrocarbons,[172] and (iii) selective catalytic reductions.[173]

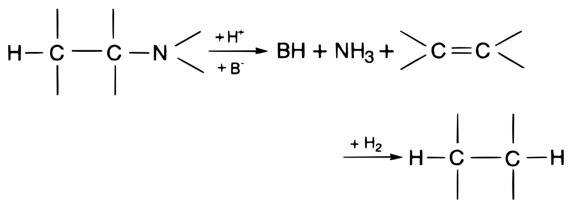
13. Hydrodesulfurization and Hydrodenitrification

Lower legislative limits on the sulfur content of gasoline are placing higher demands on hydrotreating catalysts. Thus, new active phases that are different from the conventional Ni−Mo or Co−Mo phases have attracted some interest in the past few years.

New unsupported and carbon-supported niobium sulfide and Ni-doped niobium sulfide catalysts were prepared by Allali et al.[86−88] Unsupported niobium trisulfide was found to be a better catalyst for thiophene conversion than was molybdenum disulfide. The stability of the niobium trisulfide catalyst toward reduction depended on the H_2S partial pressure under the test conditions. Either the concentration of SH groups resulting from the adsorption of H_2S on Lewis acid sites or the proton acidic properties of those groups play a key role in stabilizing the catalyst.[86] In addition to pure niobium sulfide, nikel-doped catalysts also have attracted some attention.[87,88] The catalytic activity of an unsupported mixed Ni−Nb sulfide was similar to that observed for NiMoS.

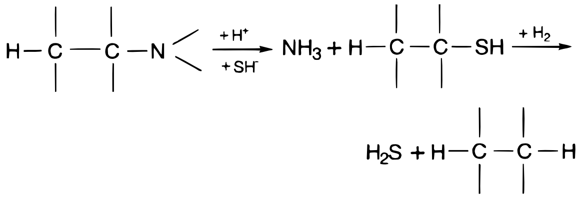
Today's environmental problems provide an impetus for the development of hydrodenitrogenation (HDN) processes. Until now, the sulfide catalysts studied have been mainly molybdenum and tungsten systems. In the HDN of pyridine, niobium trisulfide is slightly more active than MoS_2. In the *n*-pentylamine conversion, the rate of C_5 hydrocarbon formation is much higher on niobium sulfide than on molybdenum sulfide and does not vary when the H_2S partial pressure is increased 10-fold.[86]

The reactivity of a series of amines having various structures and different numbers of hydrogen atoms on the α- and β-carbon atoms was examined by Cattenot et al.[174] using four transition metal sulfides: NbS_3, MoS_2, RuS_2, and Rh_2S_3. The reaction mechanism is known to proceed via either an elimination (E2):



$$\mathrm{H{-}C{-}C{-}N}\langle \xrightarrow[+B^-]{+H^+} \mathrm{BH + NH_3 +}\ \rangle\mathrm{C{=}C}\langle \xrightarrow{+H_2} \mathrm{H{-}C{-}C{-}H} \quad (10)$$

or a nucleophilic substitution (S_N2):



$$\mathrm{H{-}C{-}C{-}N}\langle \xrightarrow[+SH^-]{+H^+} \mathrm{NH_3 + H{-}C{-}C{-}SH} \xrightarrow{+H_2} \mathrm{H_2S + H{-}C{-}C{-}H} \quad (11)$$

The relative importance of these mechanisms depends on the structure of the substrate to be transformed and on the properties of the transition metal sulfide. NbS_3 is the most active of the sulfides in the elimination reaction due to its high acidity, but it is inactive in the nucleophilic substitution.

A series of Nb−Mo carbide [$Nb_{1.0}Mo_xOC$ ($x = 0.67-2.0$)] catalysts was found to be active for quinoline HDN, and the activity did not vary much with changes in the ratio of the two metals (Mo/Nb).[75] The maximum rates of sulfur and nitrogen removal occurred on the surface oxide catalysts (niobium−aluminum) containing 5 wt % Nb_2O_5, at which composition the surface is reported to have the highest Lewis acidity.[129] The maximum activities, when normalized for surface area, occurred at a support composition of 80 wt % Nb_2O_5 for the mixed niobium−aluminum oxides. A few years ago, transition metal carbides and nitrides were found to be active for the removal of nitrogen[175] and sulfur compounds.[176] The bimetallic oxycarbide system, Nb−Mo−O−C (Mo/Nb = 0.67−2.0), was proposed to be active in the hydrodenitrogenation (HDN) and hydrodesulfurization (HDS) reactions.[75]

The bimetallic oxynitrides of type M_I−M_{II}−O−N (M_I, M_{II} = Mo, W, V, Nb, Cr, Mn, and Co) were tested in hydrogenation (HYD), hydrodenitrogenation (HDN), hydrodesulfurization (HDS), and hydrodeoxygenation (HDO) reactions using a liquid feed mixture consisting of 3000 ppm sulfur (dibenzothiophene), 2000 ppm nitrogen (quinoline), 500 ppm oxygen (benzofuran), 20 wt % aromatics (tetralin), and the balance as aliphatics (tetradecane).[177] In HYD, aromatic rings are hydrogenated without the removal of any heteroatoms, whereas HDN, HDS, and HDO totally remove N, S, and O, respectively. The bimetallic oxynitrides containing molybdenum exhibited excellent HDN activity. Molybdenum and tungsten alloyed with early transition metals (V, Nb, or Cr) were sulfur tolerant, while Mn and Co alloys were sulfur sensitive and showed bulk sulfidation.

14. Fine Chemicals and Other Catalytic Syntheses

A large quantity of poly(ethylene terephthalate) (PET) has been used to make products such as synthetic fibers, films, and bottles. An investigation by Kushimoto et al.[126] showed a new type of niobic acid to be an effective catalyst for the polycondensation reaction to form PET. Niobic acid, which was prepared by the hydrolysis of $NbCl_5$ using NaOH, was very effective, whereas that prepared using NH_4OH showed no activity.

Methyl isobutyl ketone (MIBK) is one of the most important products derived from acetone. This compound is useful not only as an organic solvent but also in the preparation of paints and chemical compounds, such as stabilizers. $Pd/Nb_2O_5\cdot nH_2O$ showed a much higher catalytic activity and selectivity in the one-step synthesis of MIBK than did $Pd/\gamma\text{-}Al_2O_3$. Furthermore, $Pd/Nb_2O_5\cdot nH_2O$ exhibited good durability during the one-step synthesis of MIBK and was highly resistant to water present in the acetone substrate. This catalyst is bifunctional: the acid sites of niobic acid catalyze the condensation of acetone to mesityl oxide while the palladium metal deposited on the catalyst surface selectively hydrogenates mesityl oxide to MIBK.[178]

The decomposition of chlorofluorocarbons (CFCs) to form harmless compounds needs to be developed to reduce global environmental pollution. It has been proposed that C−Cl bond cleavage is an important step in CFC decomposition. Morikawa et al.[171] found that the lattice oxygen of niobium oxide in a TT phase oxidized CCl_4 into CO_2 very selectively (without the formation of phosgene, $COCl_2$) according to

$$Nb_2O_5 + 2CCl_4 \xrightarrow{473K} 2NbOCl_3 + CO_2 + COCl_2 \tag{12}$$

$$2Nb_2O_5 + 3CCl_4 \xrightarrow{>573K} 4NbOCl_3 + 3CO_2 \tag{13}$$

This is in contrast to the reaction occurring on amorphous niobium phosphate in which an inner niobium phosphate participates in the complete oxidation of CCl_4 into CO_2.

For practical reasons, there is a great deal of interest in the catalytic synthesis of methanethiol via the hydrosulfurization of methanol. The main problem with this reaction is how to obtain a high selectivity to methanethiol. As the results in Table 8 show, the hydrogen form of a niobium-containing molecular sieve of the MCM-41 type with Si/Nb = 16 exhibits a high selectivity for CH_3SH even at a H_2S/CH_3OH = 1:1 molar ratio.[56,60]

15. Photocatalysis

Photoelectrochemical processes at semiconductor colloid/electrolyte interfaces, such as the splitting of water, have received special attention because of their possible application to the conversion of solar energy into chemical energy. At the end of the 1980s a new group of niobium compounds with a layered structure was synthesized. Tanaka and co-workers[180] described applying these layered perovskite type niobates, $AB_{n-1}Nb_nO_{3n+1}$ (A = K, Rb, or Cs; B = La, Ca, Pb, and n = 2 or 3), to photocatalytic H_2 evolution from an aqueous methanol solution. Some niobate layered compounds, such as $A_4Nb_6O_{17}$ (A = K, Rb),

Table 8. Reaction between Methanol and Hydrogen Sulfide at 623 K (Results for the Stationary State of the Reaction)[a]

	selectivity (%)			
catalyst	$(CH_3)_2O$	CH_3SH	$(CH_3)_2S$	$(CH_3)_2S_2$
		H_2S/CH_3OH=1:1		
H-AlMCM-41 (Si/Al=16)[b,c]	62	24		
H-NbMCM-41 (Si/Nb=16)[b]	12	88		
		H_2S/CH_3OH=2:1		
H-AlMCM-41 (Si/Al=16)[b]	57	35		8
H-NbMCM-41 (Si/Nb=16)[b]	11	84	2	3
NaY (Si/Al=2.54)	15	77	8	
HNaY[d]		3	60	

[a] Reproduced from ref 56. Copyright 1997 Elsevier Science. [b] Obtained via ion exchange of the parent material with NH_4^+. [c] ∼14% selectivity to hydrocarbons. [d] 37% selectivity to hydrocarbons.

achieved high quantum efficiencies in the overall photodecomposition of water by loading ultrafine Ni metal particles in the interlayer space.[181−185] This compound is ion-exchangeable and has corrugated niobium oxide sheets stacked along the *b*-axis of an orthorhombic unit cell. This family of compounds has a unique structural feature in that it has two different kinds of alternative interlayer spaces: (i) one in which Ni^{2+} ion intercalates and water is reduced to H_2, and (ii) another where water is oxidized to O_2. The material with the general formula: $A_4Ta_xNb_{6-x}O_{17}$ ($A = K$ or Rb; $x = 2, 3, 4$, and 6) belongs to the same family as $K_4Nb_6O_{17}$.[183]

The rates of H_2 and O_2 evolution on $Ni-Rb_4Ta_6O_{17}$ and $K_4Nb_6O_{17}$ were smaller than on $Ni-Rb_4Nb_6O_{17}$.[184,185] $H_2Ti_4O_9$ and $K_4Nb_6O_{17}$ nanocomposites intercalated with both TiO_2 and Pt were capable of cleaving water into hydrogen and oxygen, but no gas evolution was noticed in the presence of $K_4Nb_6O_{17}/TiO_2$, $K_4Nb_6O_{17}/Pt$, $H_2Ti_4O_9/TiO_2$, $H_2Ti_4O_9/Pt$, or unsupported TiO_2/Pt.[186] Recently, Abe et al.[72] studied the photoproduction of H_2 from various alcohols and found that porous niobium oxide prepared by the exfoliation of $K_4Nb_6O_{17}$ was more active in evolving H_2 from alcohols than was the original $H^+/K_4Nb_6O_{17}$ catalyst.

Niobium catalysts can be used in photooxidized processes. Propene is photooxidized on Nb_2O_5/SiO_2 catalysts obtained from different preparation methods. According to Tanaka et al.,[92] propene photooxidation on type A catalysts ($A = Nb_2O_5/SiO_2$ prepared by an equilibrium adsorption method) yields propene oxide selectively, whereas the photooxidation on type E catalysts ($E = Nb_2O_5/SiO_2$ prepared by an evaporation to dryness method) with low-loading of niobium yields propanal selectively. The propene oxide forms on monomeric NbO_4 units, while propanal is the product of propene oxide decomposition on oligomeric NbO_4 tetrahedra.[92]

2-Propanol was catalytically converted to acetone by niobium oxide supported on porous Vycor glass in the presence of oxygen or nitrogen monoxide under UV radiation.[187] NO acted as an oxidant, but the reaction rate was three times slower than when oxygen gas is used.

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