

CATALYTIC APPLICATIONS OF NIOBIUM COMPOUNDS

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Introduction

This article examines the potential uses of niobium, and its compounds, as catalysts in chemical processing. The word potential is deliberately chosen because in 1978 none of the world's twenty-five major catalysts (1) contained niobium. On the other hand, catalysts containing molybdenum and vanadium, neighbors of niobium in the periodic table, realized over 80×10^6 of sales in that same year. At the same time many of the patents for niobium catalysts cover applications in which niobium improves the activity of, or substitutes for, molybdenum based compounds. With favorable cost differentials and improvements in understanding, niobium may be able to replace molybdenum in some of its traditional uses.

The patent literature describes the types of chemical reaction for which niobium compounds have been shown to be beneficial. To understand the science behind these applications, however, it is necessary to know some of the solid state chemistry of the niobium oxides and sulphides and how it contrasts with that of molybdenum. This is outlined in the first section of the present paper. Later sections describe the known applications of niobium catalysts and an attempt is made to provide some explanation of the experimental observations. It is important to realize that catalysis is a poorly understood subject. Present knowledge consists of empirical observations of the activities and selectivities of different materials as catalysts and results of fundamental investigations of the processes which occur at the surfaces of relatively simple materials. Information about the catalytic effects of niobium compounds, is almost solely of the first type - empirical observations primarily recorded in the patent literature. Any understanding of these observations can only be gained by making comparisons with chemically and structurally related materials which have similar catalytic effects whose mechanisms have been partially explored.

At the end of this chapter some of the future possible applications for niobium are set against the future demand for catalysts by the continuously changing chemical and petrochemical industries.

Relevant Features of Niobium Chemistry

The chemical behavior of niobium is dominated by the relative stability of its oxide Nb_2O_5 , and as such, it is similar to that of its neighbors in the periodic table, zirconium, hafnium and tantalum. Molybdenum and tungsten have similar chemistries to niobium in their fully oxidized 6-valent states, but in contrast they also have a very extensive chemistry in their lower oxidation states.

	<u>Nb, Ta</u>	<u>Mo, W</u>
Common Oxidation States	5 (Oxides) 4 (Sulphides)	6,5,4,3,2 6,5,4,3,2

Nb_2O_5 is hard to reduce to NbO_2 , requiring treatment at 1000 C in pure hydrogen; on the other hand, WO_3 and MoO_3 are reduced much more readily.

Another reflection of this stability, and one that has hampered the development of niobium chemistry, is the insolubility of most of its compounds; the only commonly available salt of niobium, which is soluble in water, is the oxalate.

Oxide Chemistry

Nb_2O_5 is formed either by oxidation of niobium metal or by the decomposition of "niobium hydroxide" or niobium salts. It is a white insoluble polymorphic solid, and at least five structural modifications have been reported below 900 C². Above that temperature $\text{H-Nb}_2\text{O}_5$ is stable, but the precise structure of any sample will depend on its heat treatment and history.

Thus the properties of " Nb_2O_5 " supports or catalysts are expected to be extremely dependent on the preparative route used to make them. Little work has been reported in this important area, where the degree of understanding contrasts very unfavorably with that of the more widely used catalyst supports, SiO_2 and Al_2O_3 .

Nb_2O_5 reacts with most other oxides to form mixed oxide phases. This is of signal importance in its catalytic chemistry, where there is substantial potential for improvements in activity and selectivity through the preparation of new structures. With monovalent oxides perovskites are formed: MNbO_3 (M = Li, Na and K). Compounds with the pyrochlore structure may also be formed e.g. $\text{Cd}_2\text{Nb}_2\text{O}_7$ and KNbWO_6 . Reaction with Fe_2O_3 , MnO_2 and SnO_2 produce mixed oxides with complex structures.

The phases formed by the reaction of Nb_2O_5 and MoO_3 are of particular interest because of their use as the partial oxidation catalysts discussed later (see section "Selective Oxidation Reactions") W^{vi} , Mo^{vi} and Nb^{v} have similar ionic sizes, so that one element can substitute for the other very extensively; $\text{Nb}_2\text{O}_5:\text{MoO}_3$ mixtures exemplify the complexity of much of the solid state chemistry of niobium.

On heating such mixtures different compounds are produced depending on the relative proportions of the oxides, and the temperature used (3). New phases have been found with the following compositions, and more details can be found in Ekstrom (3).

Reaction TemperatureNb₂O₅ : MoO₃Ratio

1100 C	4:1		
700 C	4:1	2:1	1:3
Vapour Phase	6:1	7:3	
640 - 900 C	6:1	7:3	1:3

Agreement between different workers is not complete in this difficult area and it is probable that the 7:3 and 2:1 phases are really the same (7:3 = 2.3:1).

The crystal structures of these phases are based on the "tetragonal tungsten bronze" structure (4), Figure 1, in which a framework of corner-shared tungsten-centered octahedra link to form pentagonal and square tunnels which may contain ions such as Na, K or NH₄⁺. Tungsten is present as W^{vi} and W^v, and the framework has a formula [W_{1-x}^{vi}W_x^vO₃]^{x-} with xK⁺ ions (for example) filling the tunnels to maintain the charge balance. In compounds containing Mo^{vi} and Nb^v, the Mo^{vi} substitutes for W^{vi}, (Tungsten and molybdenum have similar oxide chemistries).

As an example Mo₅O₁₄ and Mo₃Nb₂O₁₄ (3 MoO₃·Nb₂O₅) are isostructural. A bronze framework contains some of the niobium ions in the pentagonal tunnels along with extra oxide ions. This gives the niobium atoms pentagonal bipyramidal coordination. Other Nb₂O₅:MoO₃ and Nb₂O₅:WO₃ compounds are probably

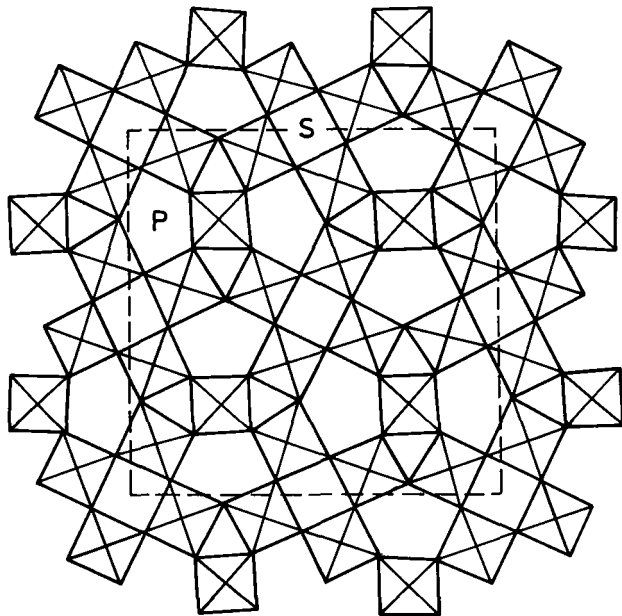


Figure 1. The tetragonal "tungsten-bronze" structure.

based on corresponding tungsten bronze structures. It is probable that this structure is highly significant, since the situation of specific niobium ions coordinated to oxygen recalls the coordination of oxygen to the bismuth ions in bismuth molybdate $\text{Bi}_2\text{Mo}_2\text{O}_9$ the selective oxidation catalyst (see section "Selective Oxidation Reactions"). In this material, which we can usefully write as $\text{Bi}(\text{Bi}_3\text{O}_2)(\text{Mo}_4\text{O}_{16})$, only a small proportion of the oxygen atoms, those coordinated to the bismuth ions, are weakly coordinated and able to participate in the oxidation process. Since these special oxygens are well separated from each other, complete combustion to CO_2 is prohibited. Similarly in $\text{Mo}_3\text{Nb}_2\text{O}_{14}$, which we can write $[\text{NbO}_2][\text{NbMo}_3\text{O}_{12}]$, we again find that there are a small proportion of the total number of oxygen ions in special sites which may be available for oxidation at low temperatures.

Maximum activity formulations of some patented $\text{Nb}_2\text{O}_5/\text{MoO}_3$ catalysts occur at $\text{Nb}_2\text{O}_5:\text{MoO}_3$ ratios of 1:2 and 1:4. This suggests that structures of the type described above may exist at the surfaces of these catalysts, and be responsible for some of their activity. Two lower oxides of niobium, NbO_2 and NbO , are known, and it has been suggested recently that the presence of the former is important when Nb_2O_5 is used as a catalyst support under reducing conditions. It has been found that the ability of iridium supported on Nb_2O_5 , to adsorb hydrogen is strongly suppressed when compared with iridium supported upon alumina, silica and a few other materials (5). This suppression may be due to electron transfer from the reduced surface cation ($\text{Nb}^{\text{d}1}$) to the supported metal, and somewhat paradoxically this is reflected in improved catalytic properties (see section "Fischer-Tropsch Syntheses"). The absorption suppression for platinum supported by titania appears also to extend to carbon monoxide, and perhaps the clue to understanding this apparent paradox lies in the finding that the CO-H_2 reaction is inhibited on metals whose heats of adsorption for carbon monoxide are too large (5).

Sulphide Chemistry

The most important niobium sulphide is the four-valent NbS_2 . Its crystal structure is based on infinite NbS_2 layers, in which the niobium atoms occupy trigonal prismatic sites between the sulphur layers:

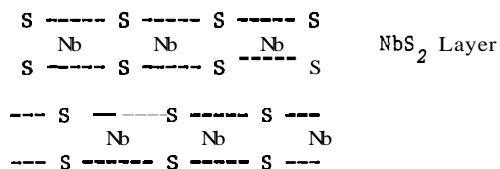
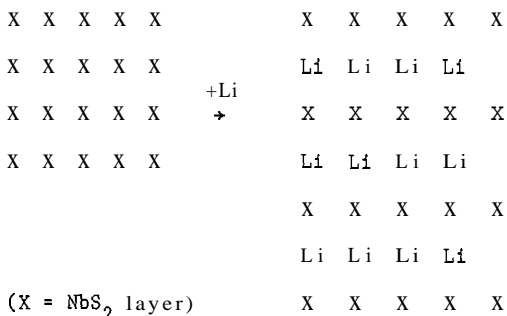


Figure 5 shows this in more detail. In three dimensions there are numerous ways in which the NbS_2 layers may be stacked relative to one another so that many polymorphs of NbS_2 have been prepared. However, one would not expect the surface catalytic activity of NbS_2 to be modified by the exact stacking sequence of the layers.

Amorphous forms of NbS_2 may be prepared in which the size of the ordered layers is reduced to about 25-50Å - these are of interest as hydrodesulphurization (HDS) catalysts.

The layers in NbS_2 are only weakly held together by (S...S) Van de Waal forces and under certain circumstances "guest molecules" may enter the (S...S) region or "intercalate" causing the lattice to expand perpendicular to the layers. The guest molecule is usually a strong electron donor such as Li, Na, NH_3 or aniline:



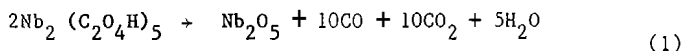
Thus intercalation has two results: it leads to a transfer of electrons from the donor to the NbS_2 layers, and it causes a change in the NbS_2 layer-layer separation. Thus the electronic differences between NbS_2 and MoS_2 , the powerful HDS catalyst could be diminished by intercalation. At the same time, the incorporation of an intercalation step in a preparation, might lead to a route for the enhancement of the specific surface area of a catalyst through explosive intercalation, or to a route to the controlled decoration of surface sites by promotor atoms.

Catalyst Formulations

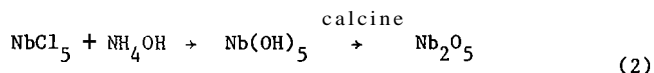
The typical catalyst has three components; the active phase, the support and the promotor. The active phase is generally the component on whose surface the primary reaction proceeds. The support is frequently a high-surface-area material on which the catalyst is deposited, and which usually allows a more cost effective use of the active phase by enhancing its dispersion (the proportion of atoms at the surface of a material). The promotor is a component whose addition to a catalyst mixture bestows some beneficial influence on its activity or selectivity. This description of the typical catalyst, although naive, is a useful background against which it is possible to discuss the use of niobium in catalysis.

In the examples of the following sections the understanding of the role of niobium, in many of the reactions discussed, is insufficient to distinguish between its presence as the primary agent or a promotor. Consequently, we need only consider that catalyst preparations involving niobium are designed to produce support materials or active phases. The properties of interest in a good support, are its surface area, its pore size distribution and the temperature dependence of these properties. In addition chemical effects, which lead to a modification of the properties of the active phase by the support, are important, although if these occur then they serve to further blur the boundaries between the components of the catalyst as discussed naively in the previous paragraph.

For some processes such as those where consecutive reactions are to be avoided, a catalyst support is required with a low surface area. More frequently, however, a high surface area is required, and it is for this purpose that the preparations of Nb_2O_5 as a support have been optimized. There are two simple routes which have been recorded in the literature. The thermal decomposition of niobium oxalate



and the precipitation of the oxide from a methanolic solution of the chloride.



Unfortunately, neither of these two routes leads to very high surfaces.

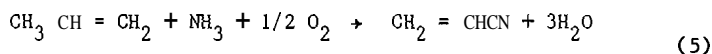
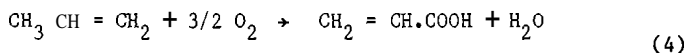
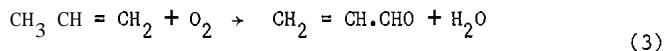
$8m^2/gm$ has been quoted as a typical value after calcination at 600 C. Recently a new route to much higher surface area material was shown to be feasible by A.E.R.E. Harwell, producing material of $75 m^2/gm$ at 600 C and $28m^2/gm$ at 900 C.

When niobium oxide is used as an active phase it is generally distributed over a support by impregnating the latter with a solution of a niobium salt, such as the oxalate, followed by drying and calcining. It would be useful to know more about the morphology of the niobium oxide prepared in this way. Knowledge of the species present in niobium oxalate solutions, how they are adsorbed by oxides, and the consequences of subsequent calcination would all be valuable aids in attempts to optimize Nb_2O_5 dispersion and activity.

Catalytic Chemistry

Selective Oxidation Reactions

Some of the most widely discussed potential applications of niobium catalysts are in selective oxidations and the related ammoxidations. The most important of these reactions commercially, are the oxidation of propylene to acrolein (1) and acrylic acid (2), and the ammoxidation of propylene to acrylonitrile (3). The market for acrylonitrile is 1.4×10^9 Kg per year, an amount which is mainly used in fibres and resins. These three reactions are



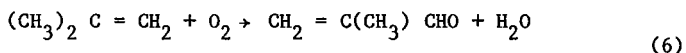
The original catalysts developed for these processes by Sohio were based on bismuth molybdate. They are used at between 452 and 510 C in the 1-3At pressure range, either in fixed or fluidised beds.

Most of the references to the use of niobium as a catalyst component in selective oxidation reactions detail the improvement in selectivity brought about by the presence of niobium. Present catalysts are far from perfect since large quantities of material end up as the unwanted products of total combustion, CO and CO₂, or other oxidation products such as acetic acid.

Typical values for the selectivity of feedstock conversion in the preparations of acrylonitrile (7) or acrolein (8) are 70 percent or 85 percent respectively, and, as we will discuss later, the oxidations of higher molecular weight olefins result in even poorer selectivities.

As an example of what has been claimed, US patent 3,557,199 (9) teaches that high selectivities of production of acrylic and methacrylic acids from their respective aldehydes can be obtained using niobium catalysts. The reaction requires a catalyst with a niobium to molybdenum atomic ratio between 0.5:1 and 2:1 i.e. between Nb₂O₅.2MoO₃ and 2Nb₂O₅.MoO₃. At 417 C, 77 percent conversions of acrolein were attained with 81 percent selectivity; 4.0 percent acetic acid and 38.0 percent CO and CO₂ were obtained. The examples in the patents show that although the selectivity is high for these niobium to molybdenum ratios, it is only achieved, however, at the expense of a large amount of total combustion. (N.B. The percentage yields are values of moles of product per mole of acrolein converted, times 100%, and therefore, the sum can be more than 100%).

Another example is included in the patent awarded to the Asahi Glass Company (9). This starts from the position that the oxidations in equations 1-3, although successful for propylene, are much less attractive for the oxidation of higher molecular weight homologues such as the conversion of isobutylene to methacrolein. (Methacrolein, in turn, is oxidized to methacrylic acid which can be esterified to methylmethacrylate. The use of this material under trade names such as Plexiglass amounts to greater than 300,000 tons per annum in the USA).



In this reaction selectivities of 50 percent rather than the 85 percent for propylene are common. In consequence, this route to methylmethacrylate is not yet widely used, but since it is potentially attractive when compared with the conventional route from acetone and hydrogen cyanide, with superior catalysts it may become the normal process. The Asahi work teaches that incorporation of niobium into a bismuth molybdate catalyst leads to much higher yields of methacrolein. For example, a catalyst of atomic ratios Mo:Bi:Nb of 12:9:3 leads to conversions of isobutylene of 96 percent with a selectivity of 74 percent. This yield is compared with the yields of the 2 component materials in Table I below.

Some insight into the behavior of niobium as a promotor comes from work in which the influence of niobium on the selectivity of oxidation of propylene to acrylic acid was investigated (10). A niobium oxide-molybdenum oxide catalyst supported on silica was used, and the variation of yield with niobium content is shown in Figure 2. It can be seen that a volcano curve is obtained in which the maximum conversion occurs at an atomic ratio of niobium

Table I. Conversions of Isobutylene to Methacrolein over Niobium Catalysts

	<u>Conversion</u> %	<u>Selectivity %</u> for Methacrolein	<u>% CO + CO₂</u>
Mo ₁₂ Bi ₉	71.5	69.9	24.8
Mo ₁₂ Nb ₃	82.6	65.8	29.1
Mo ₁₂ Bi ₉ Nb ₃	96.1	74.4	22.7
Mo ₁₂ Bi ₉ Nb ₃ Te ₁	95.0	76.7	18.4

(Conversions of propylene to acrolein were found to be)

Mo ₁₂ Bi ₉ Nb ₁	95.3	79.1	13.8
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(It can be seen that part of the improvement in performance is brought about by reducing the proportion of feedstock undergoing complete combustion.)

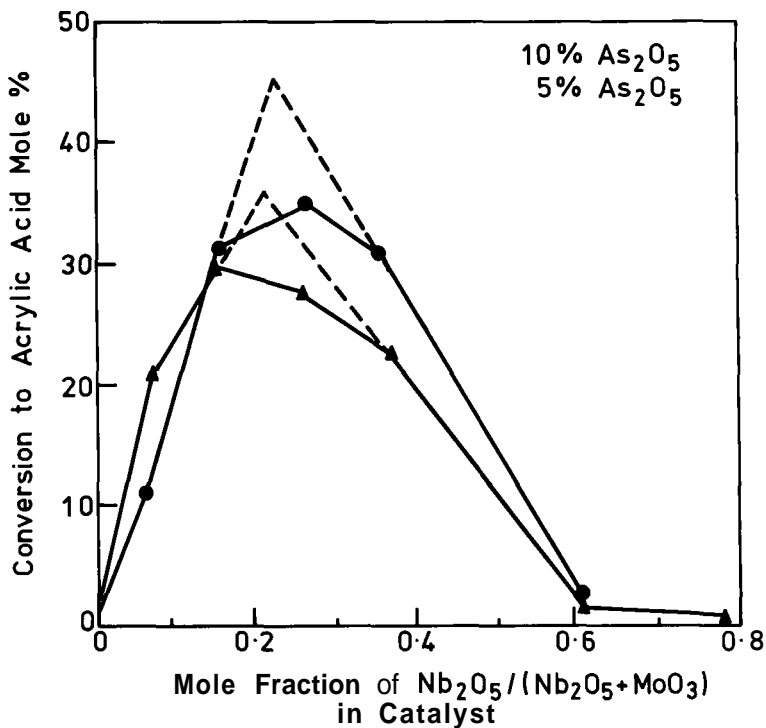


Figure 2. Effects of Nb₂O₅/MoO₃ ratio and As₂O₅ on conversion of propylene to acrylic acid. Conditions 400 C, 2.4s contact time, propylene: air: steam ratio 1:75:3.

to molybdenum of 1:2. Since an analogous curve occurs for bismuth molybdate catalysts (see Figure 3 (11)) it is worth recapping how this material is thought to function. The fundamental reaction is the reversible oxidation-reduction process which takes place at its surface. The catalyst oxidizes the hydrocarbon, and then incorporates fresh oxygen from the gas phase within its lattice. One model of the mechanism assumes that oxygen vacancies on the molybdate groups act as electron acceptor sites to which the propylene can adsorb and form an allylic intermediate. Oxygen is then transferred from the lattice to the allyl group, which then desorbs as acrolein. Fresh oxygen coming in from the gas phase replaces the lost lattice oxygen, although not via a simple substitution, since the initial anion vacancy is firstly filled by diffusion from the bulk. An important aspect of these catalysts is that they cause one stage oxidation without bringing about total combustion; effectively the reaction stops half-way. A largely accepted mechanism for this, is one based on site isolation. The oxygen that is donated by the lattice to the allyl intermediate can only come from a small number of weakly bound sites. The larger number of strongly bound oxygen atoms provides a reservoir from which the transferred oxygen atom is replaced. The weakly bound oxygen atom may be those associated with a cation vacancy, and in confirmation of this theory, the activity of $\text{Pb}_{1-3x}\text{Bi}_{2x}\text{MoO}_4$ rises rapidly with the concentration of x ¹². See Figure 4.

The precise reasons for enhanced activity at particular stoichiometries continue to be elusive, although the experimental evidence does suggest that fast oxygen transport through the lattice and readily removable oxygen atoms are important requirements. In the $\text{Bi}_2\text{Mo}_2\text{O}_9$ catalyst the bulk structure

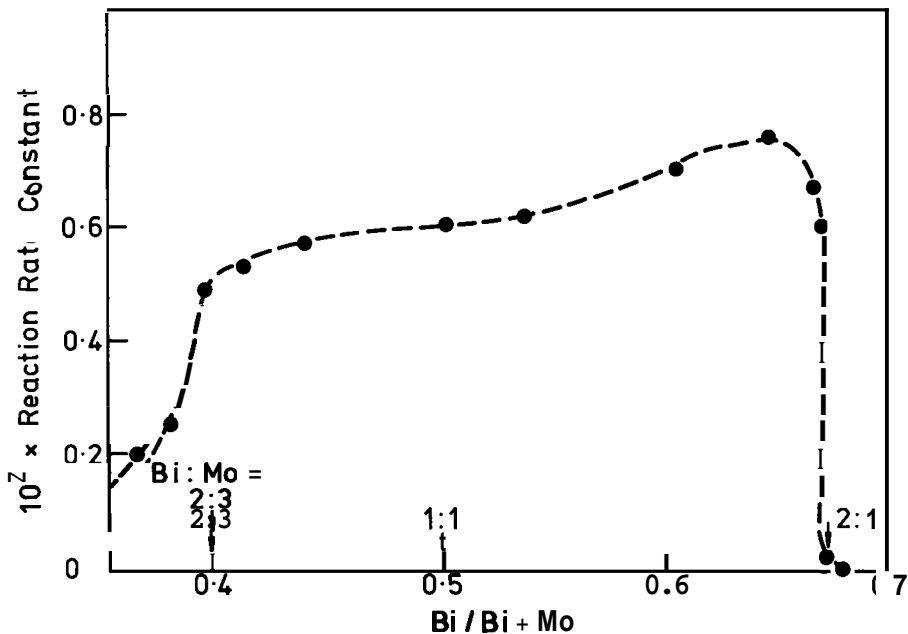


Figure 3. Butene oxidation activities of bismuth molybdate catalysts.

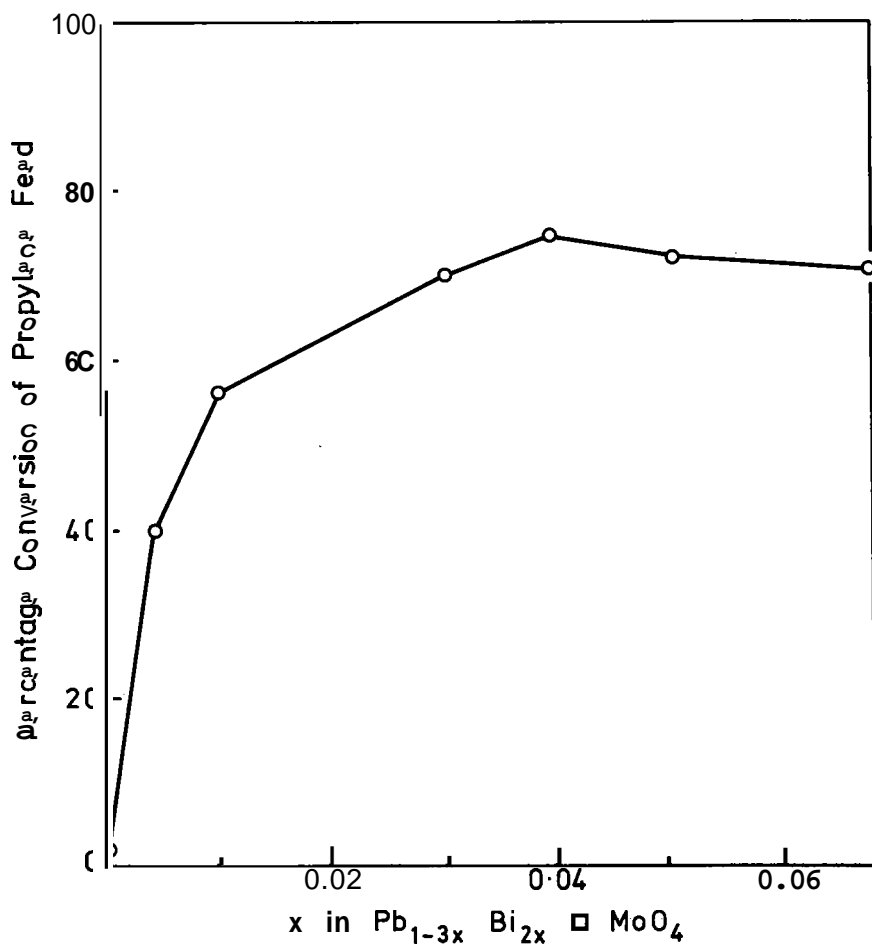
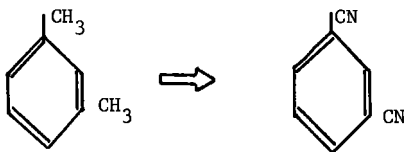


Figure 4. Ammoxidation of propylene over $PbMoO_4$ doped with Bi^{3+} .

contains particular oxygen atoms surrounded by an incomplete bismuth coordination sphere, such that at the surface, this oxygen may be coordinated by 3 bismuth ions and 1 bismuth vacancy. It is believed that this oxygen is the one responsible for the oxidation process, and it is reasonable to expect that in the active molybdenum-niobium catalysts, similar defect associated oxygen atoms may be present.

The above paragraphs are a condensation of a large corpus of kinetic and structural knowledge concerning bismuth molybdate catalysts. In contrast, it is difficult to discuss the mechanisms of niobium catalysts since it is rare in either the academic or the patent literature to find any reference to the particular phases of the niobium compounds that may be present. In the published work on iso-butylene oxidation, for example, $\text{BiMo}_{1.33}\text{O}_{5.5}$ has good activity and so also has $\text{NbMo}_{4}\text{O}_{14.5}$. Structural work on these catalysts would probably repay handsomely the efforts involved. Another point to emerge from the work of reference (10) is the observation that arsenic oxide is a very valuable promoter preventing the further oxidation of acrylic to acetic acid. A proposed explanation for this effect was that the arsenic oxide was adsorbable on two sites present at the surface of the "niobium molybdate" catalysts. One of these, the less active, led to acrylic acid; the other which had a strong affinity for arsenic oxide, led to a subsequent oxidation of the acrylic acid to carbon monoxide and carbon dioxide. Hence, as the arsenic oxide content rose, so the conversion to by-product diminished. However, eventually a concentration was reached at which those sites producing acrylic acid were also being poisoned and so the yield of this material fell also.

One further example of improvements in selectivity arising from the incorporation of niobium in a catalyst has been published by Sun Ventures, Inc. (13). They worked on the problem of enhancing the selectivity of production of dinitriles, rather than mixtures of dinitriles and mononitriles, from substituted aromatic hydrocarbons. For instance, isophthalonitrile made on the scale of a few thousand tons per annum in the U.S.A., is made by ammoxidation of meta-xylene.



(7)

High yields of the dinitrile can be obtained with a vanadium alkali metal bronze promoted with niobium.

Finally, the use of niobium oxide to promote vanadium pentoxide, (14) a catalyst for the oxidation of orthoxylene to phthalic anhydride, has been studied. It is interesting that this catalyst is one of the few, containing mixtures of niobium oxide with other oxides, for which relevant phase diagram information is available (15). These diagrams show that at temperatures less than 648 C, V_2O_5 , Nb_2O_5 and $\text{V}_2\text{O}_5 \cdot 9\text{Nb}_2\text{O}_5$ are stable phases. However, the position of the peak in the activity plot shown in Figure 5 at 40 percent V_2O_5 suggests that the formation of the mixed compound is not the sole influence at work; X-ray diffraction evidence showed that additional unknown phases were present which were at their maximum concentration at 30 percent V_2O_5 . The authors suggested that the formation of $\text{V}_2\text{O}_4 \cdot 2\text{Nb}_2\text{O}_5$ could also be

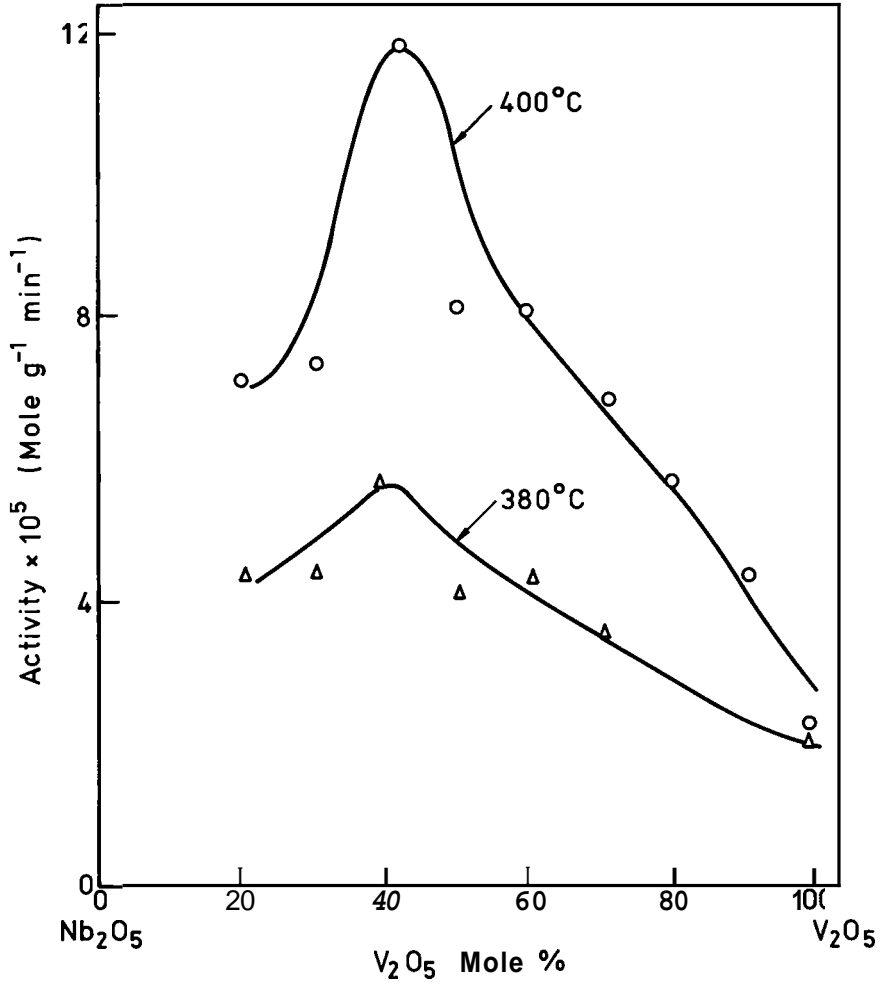
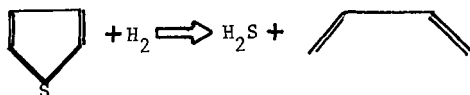


Figure 5. Variation of the activity of $V_2O_5 - Nb_2O_5$ as a function of composition.

responsible for the increase in activity. The suggestion was supported by their chemical analyses which showed the V^{1V} content to amount to 35 wt. percent of the vanadium content of the spent catalyts.

Hydrodesulphurization

Hydrodesulphurization, or H.D.S. as it is commonly called, is the reaction in which sulphur-containing materials are removed from hydrocarbon feedstocks. The necessity for this is two-fold. Firstly, downstream processing catalyts used in the manufacture of ammonia are readily converted to inactive sulphided nickel. Secondly, it is important to remove sulphur from materials which would ultimately be used as fuels, for both pollution and combustion reasons. The general reaction involved can be typified by the hydrodesulphurization of thiophene, a model compound which is used in a large number of hydrodesulphurization studies

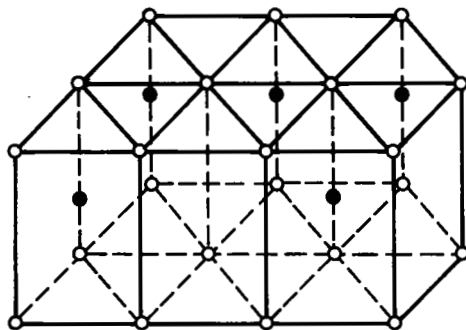


(8)

Hydrogen sulphide, produced in the reaction, is generally removed by an adsorption tower full of zinc oxide. A requirement of a catalyst for this reaction is that it must be resistant to sulphidation, either by virtue of being inert, or because it is already sulphided. The most common catalyst used is molybdenum sulphide supported on γ -alumina and promoted with cobalt, although tungsten sulphide promoted with nickel is also encountered together with other mixtures of the four materials. The catalyst is usually formed "in-situ" from the supported mixed oxides.

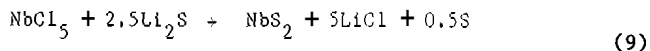
The relevance of this reaction to niobium chemistry is that molybdenum sulphide and niobium sulphide have similar crystal structures. They are both essentially two-dimensional lattices whose individual sheets comprise metal atoms surrounded above and below by layers of sulphur atoms such that the coordination around each metal atom is trigonal prismatic. See Figure 6. Since the structures are layer like, the surface is differentiated into that formed by the basal and the prismatic planes. In the prismatic planes there is a certain density of sulphur vacancies at any partial pressure of hydrogen and it is at these sites that it is thought that the centers of hydrodesulphurization activity reside, where sulphur containing molecules are adsorbed and decomposed. The simplest requirements for high activity are therefore high edge-plane areas and high vacancy densities.

In niobium sulphide it is not clear if either of these factors is limiting, and up to very recently, little work had been performed on niobium sulphide because it was not available in a high surface area form. Preparations of niobium sulphide were carried out by synthesis of the material from its constituent elements at temperatures in excess of 1000 C. A recent publication, however, has shown that niobium sulphide and other similar materials can be prepared at ambient temperatures in non-aqueous solvents. Chianelli and co-workers (16) used the metathesis reaction between niobium chloride and lithium sulphide in organic solvents such as tetrahydrofuran.

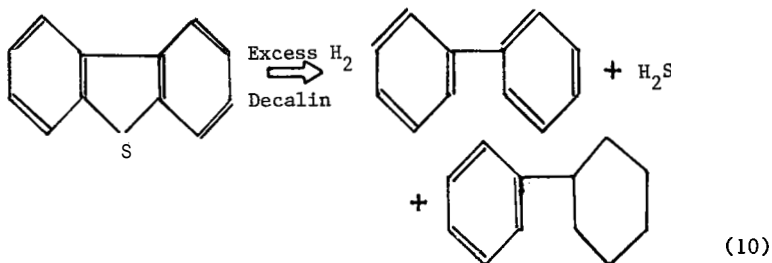


○ = S
● □ Mo or Nb

Figure 6. Structure of molybdenum and niobium sulphur MS_2 layers.

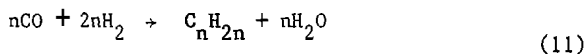


The same investigators also measured the activity of this and other materials in a model hydrodesulphurization reaction using dibenzothiophene. This is converted to biphenyl and cyclohexyl benzene at 300 C and 18Atm., and is a better model reaction than thiophene hydrodesulphurization, if one wishes to simulate the reactions that occur in the hydrodesulphurization of residual fuel oils.



It was shown that of the unsupported metal sulphides, the niobium sulphide produced in this way had medium activity. The activity ranking was: supported commercial catalysts \gg $ReS_2 \gg MoS_2 > Cr_2S_3 \gg WS_2 \sim TiS_2 \sim NbS_2 \sim VS_2 > ZrS_2 \sim MnS$. The material produced by this non-aqueous synthesis was essentially amorphous but Chianelli and co-workers also showed that at 400 C both molybdenum sulphide and niobium sulphide prepared by this route had superior activities to materials prepared by direct synthesis or thermal decomposition. The reason for this is unclear since it would be expected that materials prepared by these different routes would be similar at equal temperatures. There is no information in the patent on the surface areas of the catalysts used in the tests and therefore, it is not clear whether the intrinsic activities of the materials investigated are different, and also it is not clear whether the materials have the potential for further improvement.

These processes are currently being investigated with great enthusiasm, since they provide a route from CO and H₂ to olefins



The technical feasibility of the syntheses was demonstrated in Germany in the thirties, but there has been no incentive to use the process widely in recent years, because of the plentiful supply of olefins from cheap petroleum sources. Now, however, the picture is changing and chemical industries based on coal feedstocks are expected sooner or later to replace the increasingly expensive oil based ones. Today the processes are only used commercially in South Africa where there are plentiful supplies of cheap coal from which CO and hydrogen (synthesis gas) can be made. The international importance of the Fischer-Tropsch reactions is reflected by the many research papers and patents that are now regularly appearing on this topic. The process has traditionally used iron based catalysts and those in operation in South Africa use this metal. Precious metals have also been shown to possess activity, and in particular ruthenium has been widely investigated. A recent patent from the Exxon laboratories (6) has shown the attractive improvement in the yield of high molecular weight olefins, rather than methane, when niobium pentoxide, instead of alumina, silica or carbon, is used to support the ruthenium. The olefins produced are valuable intermediates for plastics, rubbers, alcohols, etc. Using an H₂:CO ratio of 3:1 at 103KPa they found that a 1 percent Ru/Nb₂O₅ catalyst led to an olefin yield of 59 percent, which compared with 34 percent and 13 percent obtainable with alumina and silica respectively. A selection of the results they obtained is recorded below.

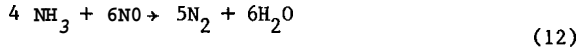
Table II. Yields of Different Products in Fischer-Tropsch Reactions

Catalyst	Temperature °C	Conversion %CO	Yield Mole. %			
			CH ₄	>C ₂	C ₂ H ₆ C ₂ H ₄	C ₃ H ₆ C ₃ H ₈
Ru	226	3.5	96	4	0	0
1%Ru/SiO ₂	232	4.1	a7	13	7	4
1%Ru/Al ₂ O ₃	228	8.8	66	34	12	8
1%Ru/Nb ₂ O ₅	244	5.7	41	59	14	11
1%Ru-Ta ₂ O ₅	226	10.3	42	54	10	16
1%Ru/V ₂ O ₃	259	1.4	49	51	21	16.5

The relationship of this fortunate catalytic behavior, to the properties of niobium oxide, has been referred to earlier.

Nitric Oxide Removal from Boiler Stack Gases

In Japan and California the electricity generating authorities have been obliged to invest in processes which will lower the NO_x concentrations in their power station boiler emissions. In Japan approximately 25 systems were operating in August 1978 of which 22 were catalytic. They used the reaction between ammonia and NO_x , which produces nitrogen and steam at temperatures between 300 and 400 C.



The most popular catalyst for this process is V_2O_5 supported upon titania, a combination which is unaffected by up to 2000 ppm of SO_2 or 100 ppm of SO_3 , important poisons of other systems. For coking furnaces, calcination plants and the like, emissions are at temperatures less than 300 C, so that there is an important requirement for catalysts which are active at lower temperatures, if heating of the emissions is to be avoided. It has been found that catalysts containing niobium are particularly successful at meeting this requirement. For example, U.S. patent 4, 131, 643 shows that a catalyst manufactured by impregnating alumina with an oxalic acid solution containing vanadium, niobium and copper followed by calcining at 400 C was capable of bringing about removal of NO at temperatures more than 100 C lower than catalysts which did not contain niobium. Figure 7 shows the percentage conversion of NO as a function of temperature for a number of different compositions. From the patent it is not clear whether the niobium is capable of bringing about the reaction independently, i.e., whether it is an effective catalyst in its own right, or whether it acts solely as a promotor.

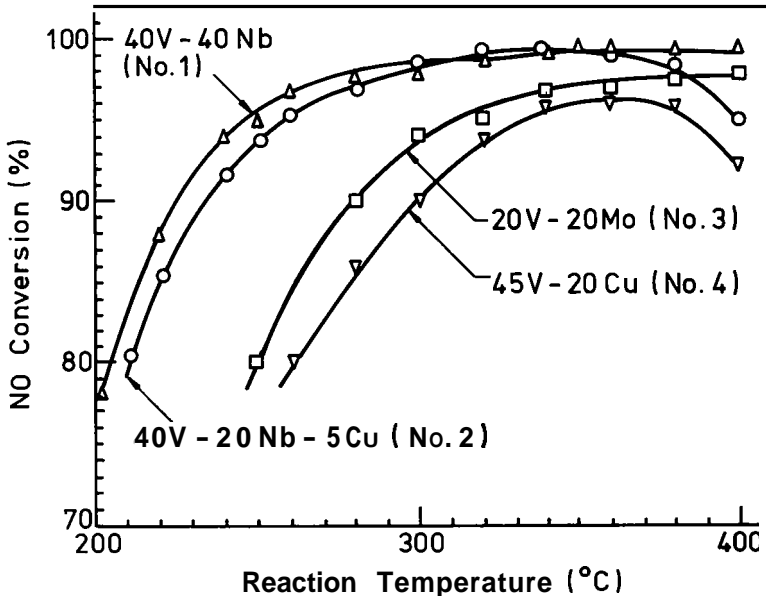


Figure 7. Relationship between NO_x conversion and reaction temperature for catalysts with and without niobium.

The Future

The reactions for which niobium catalysts have been patented are primarily those which are going to continue to be of industrial importance for decades to come. Hydrodesulphurization will become progressively more complex and will place progressively increasing demands on catalysts as the molecular weights and the concentrations of the sulphur bearing hydrocarbons in petrochemical feedstocks increase. Hydrodenitrogenation and demetallization will become equally important as the trend towards exploiting residual oils and coal liquids continues. An alternative route to chemicals from coals will be via gasification and the reactions of carbon monoxide and hydrogen. The interesting results on the use of niobium oxide as a support in the Fischer-Tropsch reaction, suggest that there may be other CO/H₂ reactions where niobium supports confer additional advantages. Finally the selective oxidation reactions are unlikely to change much before the end of the century, since the demand for commodity fibres and plastics is unlikely to be greatly influenced by the arrival of new products. So much for the market opportunities, what research should be done? As a support, much can probably be made of the new route to high surface area niobia. Recent experiments in a number of fields have shown that important surface properties such as sintering rate, poison resistance, and intrinsic activity can be influenced by varying the support under a catalyst. There are many valuable and interesting experiments to be done to decide how niobia compares with conventional materials under different conditions.

The promotion of niobium catalysts by other additives has also received little attention. The sulphide for example is readily intercalated by a variety of electron donors e.g. amines, Na, K, SnS₂, and Cobaltocene. These provide both an interesting way to modify the electronic properties of the host, and also active centers at which other reactions in a consecutive sequence can be initiated. In hydrodesulphurization the addition of cobalt to a molybdenum based catalyst results in a considerable increase in its activity. It is not too clear how this occurs, but it may be because the cobalt enhances the rate of dissociation of molecular hydrogen. If this is correct then cobalt should also promote the H.D.S. activity of niobium catalysts. Experiments in this area should definitely be tried.

Finally, and at the risk of repeating what has already been said on a number of occasions in this article, it is important to learn more about the crystal structures of the catalytically active mixed oxide phases containing niobium. Only when their structures are known, will it be possible to modify their properties in a logical manner.

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