

**CATALYTIC
PROPERTIES OF
NIOBIUM
COMPOUNDS**



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Contents

Introduction	1
1 - Dehydrogenation and Oxidative Dehydrogenation	1
2 - Ammoxidation Process and Synthesis of Alkylpyridines	2
3 - Reforming of Hydrocarbons	2
4 - Production of Polyester and Esters	3
5 - Polymerization	3
6 - Metathesis and Isomerization of Olefin	4
7 - Decomposition of Nitrogen Oxides	4
8 - The Catalyst Electrode for Fuel Cell	5
9 - Hydrocarbon Synthesis from CO and H ₂	8
10 - Hydrogenation	10
11 - Oxidation	10
12 - Miscellaneous	13
Acknowledgment	15
References	15

FIGURES AND TABLES

Fig. 1 - Reduction of NO _x with NH ₃	6
Fig. 2 - Current-potential curves	7
Fig. 3 - Activity of nickel catalysts	9
Fig. 4 - H ₂ chemisorption vs temperature of activation for supported-iridium catalysts	11
Table 1 - Oxydehydrogenation of Ethane	21
Table 2 - Oxidative dehydrogenation and dehydrogenation hydrocarbons	22
Table 3 - Ammoxidation of Hydrocarbons	23
Table 4 - Synthesis of Alkylpyridines at 450°C	24
Table 5 - Reforming of naphtha	24
Table 6 - Polyester production reaction at 280°C	24
Table 7 - Polymerization of 1,3-butadiene	25
Table 8 - Polymerization of propylene	25
Table 9 - Conversion of hydrocarbons	25
Table 10 - NO _x + NH ₃ reaction NO:300 ppm, NH ₃ :450 ppm, SO ₂ :500 ppm, O ₂ :15%	26
Table 11 - Pt-Nb Electrode	26
Table 12 - Fischer-Tropsch Synthesis	26
Table 13 - Selectivity of several Ru catalysts	27
Table 14 - Hydrogenation of benzene at 160°C, 50 atm H ₂	28
Table 15 - Production of methacrylic acid oxidation of methacrolein	28
Table 16 - Fluorination of benzotrighloride	29
Table 17 - Synthesis of diamond	29
Table 18 - Polymerization of Acetylene to Benzene	30

Introduction

This is a report prepared for CBMM, which outlines the catalytic activity and selectivity of niobium compounds including niobium oxides, salts, organometallic compounds, etc. The application of niobium compounds as catalysts to diversified reaction as seen in the content of this report is realized. The nature and action of niobium catalysts are characteristic and sometimes anomalous, suggesting the necessity of basic research and the potential use as catalysts for important processes in chemical industry.

1 - Dehydrogenation and Oxidative Dehydrogenation

The catalytic dehydrogenation or oxidative dehydrogenation of hydrocarbons has become of major industrial importance for the production of diolefins or aromatic vinyl compounds. However, the oxidative dehydrogenation of paraffin hydrocarbons has not been so successful. Recently, Thorsteinson et al.⁽¹⁾ developed an effective catalyst for the production of ethylene from ethane by the oxidative dehydrogenation process. The catalysts consist of a mixture of the oxides of Mo and V with a variety of third metals. Among the most effective catalysts found were an unsupported material having the atomic composition $\text{Mo}_{0.73} \text{V}_{0.18} \text{Nb}_{0.09}$ and a material with the composition $\text{Mo}_{0.61} \text{V}_{0.31} \text{Nb}_{0.08}$ when supported on α -alumina. The activity and selectivity are shown in Table 1. The product over MoVNb catalyst at the temperature around 300°C was exclusively ethylene at 1 atm, but at higher pressure ($\cong 20$ atm), acetic acid was obtained (selectivity $\cong 20\%$). In the reaction at 1 atm., molybdenum oxide itself has only a slight activity. The addition of vanadium does not increase the activity of MoO_3 very much, but additions of both vanadium and niobium result in a very active and highly selective catalyst. Thus, the role of niobium in this system is important to obtain high activity and selectivity.

In the patent literatures, catalysts containing niobium compounds (mainly oxide) are reported to be effective for the oxidative dehydrogenation of ethylbenzene, ethylpyridine or diethylbenzene, butenes or butane and dehydrocyclization of n-heptane to toluene.^(2,6) The data are summarized in Table 2.

In the dehydrocyclization of paraffin, cerium oxide is known as a promoter to improve the activity and selectivity of $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$ catalyst, but niobium oxide was more effective for that purpose.⁽⁷⁾

2 - Ammoxidation Process and Synthesis of Alkylpyridines

The use of vanadium oxides as catalysts in ammoxidation processes is well known. While less common, niobium oxides have also been reported for use in certain ammoxidation procedures. For example, Japanese patent No. 43-7610 discloses that unsupported catalysts consisting of mixtures of niobium oxide with tin or titanium oxide are useful for ammoxidation of alkyl substituted aromatic hydrocarbons to nitriles. For the ammoxidation of alkyl substituted aromatic compounds, the catalysts consisting of TiO_2 , V_2O_5 , Nb_2O_5 , P_2O_5 , K_2O , Cs_2O were reported to be effective for the production of terephthalonitrile from p-xylene and ammonia.⁽⁸⁾ An α -alumina supported vanadium alkali metal bronze promoted with niobium is also known as an effective catalyst for the synthesis of terephthalonitrile.^(9, 10) For the production of unsaturated nitril such as acrylonitril from alkane and alkene molecules, the catalyst consisting of MoO_3 , Nb_2O_5 , P_2O_5 etc. were reported.^(11, 12) The mixture of n-butenes and isobutene is also reported to be oxidized with air, NH_3 , and H_2O at 400°C over W , Nb , Ca , Bi , $\text{Mo}/\text{Al}_2\text{O}_3$ or $\text{Mo}_{1.5}$ Bi_1 $\text{W}_{0.3}$ Ca_6 $\text{Nb}_{0.7}$ to give 1,3-butadiene and methacrylonitril. The conversions of n-butenes and isobutene were 93-95% and 92-96%, respectively and the selectivities for 1,3-butadiene and methacrylonitrile were 83-84% and 84%, respectively.⁽¹³⁾ In the case of the reaction of propylene and nitric oxide to produce acrylonitril, $\text{Bi}_2\text{O}_3\text{-Nb}_2\text{O}_5\text{-P}_2\text{O}_5$ catalysts were reported in a U.S. patent.⁽¹⁴⁾ The data of ammoxidation are summarized in Table 3. For the production of alkylpyridines from acetaldehyde and ammonia, silica-alumina catalysts with Nb oxide, Sb oxide or Ta oxide as a promoter have been reported as shown in Table 4.⁽¹⁵⁾

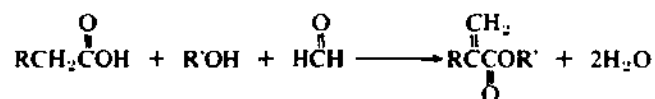
3 - Reforming of Hydrocarbons

As a reforming catalyst, platinum supported on Al_2O_3 is well known. To improve the catalytic property of $\text{Pt}/\text{Al}_2\text{O}_3$, many kinds of additives have been examined until now. In the patent literature, it was reported that the high octane value was obtained if niobium was added to Pt, Ir, Cl/ Al_2O_3 catalyst in the reforming system.^(16, 17) A Russian patent mentions that petroleum undergoes cracking over Nb, K/support at 775°C to form ethylene (32.0%), propylene (11.6%), butadiene (3.5%), and butenes (3.9%).⁽¹⁸⁾ The other patent stated that the addition of Nb or Ta and F to $\text{Pt}/\text{Al}_2\text{O}_3$ was effective for the hydrocracking of n-heptane.⁽¹⁹⁾ The data are shown in Table 5.

4 - Production of Polyester and Esters

Polyesters such as polyalkyleneterephthalate are produced by the condensation reaction of terephthalic acid derivatives. Halogenated niobium compounds are known to show a high catalytic activity for this condensation. However, in some cases, the coloration of polyester products occurs by a side reaction with halogen compounds. To avoid the coloration, the hydrolyzed NbCl_5 was used as a catalyst in the reaction of dimethylterephthalic acid.⁽²⁰⁾ The hydrolyzed catalyst showed high activity and the product had high clarity. Niobium metal powder was also used to produce colorless polyester.⁽²¹⁾ For the condensation of glycol ester, niobium or tungsten aryloxides are known to show high catalytic activity.⁽²²⁾ The data are summarized in Table 6.

As for the synthesis of esters, acrylic ester was obtained from aldehyde, aliphatic carboxylic acid, and aliphatic alcohol at 300°C over Nb_2O_5 (10 wt%)/ Al_2O_3 .



With the molar ratio (2:1) of HCHO to CH_3CHO and that (1.9:2) of CH_3OH to CH_3COOH and with 1.2 of flow rate, 31% (based on acetic acid) of methyl acrylate was obtained.⁽²³⁾ Methyl acrylate was also obtained directly from formaldehyde and methyl acetate with Nb_2O_5 (10 wt%)/ Al_2O_3 , the yield being 14%.⁽²⁴⁾ Ethyl acrylate can be obtained at 315°C from acrylonitril, water, and ethanol when Nb_2O_5 (10wt%)/ SiO_2 is used as a catalyst.⁽²⁵⁾ Methyl succinic acid mono and dimethylester is reported to be formed at 150°C from propylene (6 atm), CO (40 atm), O_2 (20 atm) and CH_3OH with a catalyst consisting of Nb methylate, Cu acetate, KBr, and $\text{P}(\text{C}_6\text{H}_5)_3$.⁽²⁶⁾ The effect of Nb is much better than that of Ta or Ti. Diacetoxy butene is reported to be formed from butadiene, sodium acetate, and acetic acid at 80°C over $\text{Pd}_6\text{S}_{15}\text{Nb}_3 \text{C}_{1000}$, the selectivity being 85%.⁽²⁷⁾

5 - Polymerization

Niobium compounds are known as polymerization catalysts for the polymerization of olefin or diolefin. For example, a mixed catalyst of niobium trichloride distearate, nickel naphthenate and triethylaluminium can initiate the polymerization of 1,3-butadiene to obtain a liquid polymer.⁽²⁸⁾ The $\text{Nb}(\pi\text{-C}_3\text{H}_5)_3$ catalyst polymerizes butadiene at 30°C to yield 50% of polybutadiene, the microstructure being 100% of 1,2-type.⁽²⁹⁾ In the case of $\text{TiCl}_2\text{I}_2 + \text{Al}(\text{iC}_4\text{H}_9)_3$, however, the yield is 20% at 50°C and 92% of the microstructure is

1,4-cis type. For the polymerization of butadiene in aqueous emulsion state, Nb(IV) ion has polymerization activity as shown in Table 7. ⁽³⁰⁾

As a catalyst for the polymerization of olefin, Ziegler-Natta catalyst is very well known. The addition of metal halide to the Ziegler-Natta catalyst is reported to improve the activity and the crystallinity of produced polymers. ⁽³¹⁾

For the copolymerization of ethylene and propylene, the mixture of tetraaryl niobium and halogenized titanium was used as a catalyst. ^(32,33) From ethylene (45 g) and propylene (110 g) mixture under high pressure (22 atm.) at 70°C, 55.4 g of gummy polymer was obtained. Niobium tetrachloride butanoate was also active for the polymerization of cyclic monoolefins. ⁽³⁴⁾

6 - Metathesis and Isomerization of Olefin

A catalyst active for the olefin reactions including olefin disproportionation which comprises a compound of niobium or vanadium complexed with NO and a selected complexing agent (e.g. benzoic acid) and combined with an organoaluminum compound (e.g. methylaluminum sesqui-chloride) was reported. ⁽³⁵⁾ Niobium oxide is also active for the propylene metathesis at a high temperature (538°C). ⁽³⁶⁾

On the other hand, by using NbF₅ as a catalyst, a variety of hydrocarbon products was observed from the mixture of n-hexane and cyclohexane even at moderate temperatures ($\approx 50^\circ\text{C}$). ⁽³⁷⁾ The mechanistic study of n-hexane homologation over Nb metal was also reported. ⁽³⁸⁾ The data are summarized in Table 9.

1-Hexene and 1-heptene are isomerized at 300°C with niobium hydride supported on SiO₂ to give 2-hexenes and 2-heptenes, respectively. ⁽³⁹⁾

7 - Decomposition of Nitrogen Oxides

The catalysts for the decomposition of NO_x in the industrial stack gas are very important to prevent the air pollution. In some cases, for the gases which do not contain SO_x or dust, the catalyst systems are practically working in the industrial plant using NH₃ as a reducing reagent. The most popular catalyst for this process is V₂O₅ supported on TiO₂ which shows the practical activity at temperatures between 300 and 400°C. However, for coking furnaces or calcination plants in steel industry, the catalyst which possesses low temperature activity is demanded, because the emission gases are at temperatures lower than 300°C.

The addition of Nb to the practical catalyst seems to be very effective to improve the low temperature activity in such a system. Japanese patents⁽⁴⁰⁻⁴³⁾ showed that the catalyst containing Nb was very active at low temperatures (<200°C) compared to that without Nb component as shown in Fig. 1 and Table 10.

The addition of Nb is effective not only for the catalytic activity but also for the stabilization of catalyst at high temperature treatment to remove the byproducts such as acidic ammonium sulfate which deposited on the catalyst surface in the reaction.^(44, 45) The addition of Nb is also effective to improve the mechanical strength of the catalyst.⁽⁴⁰⁾ The catalyst which contains, V, Nb and other components of Ti, Cu, Cr, W, Mo, Fe, Ni (at least one metal component of this group) showed high catalytic activity at low temperature region and also has the activity for the decomposition of excess unreactive NH₃ gas.⁽⁴¹⁾ The catalyst for the direct decomposition of NOx without reducing reagent is reported in Japanese patent.⁽⁴⁶⁾ NOx should be decomposed to N₂ and O₂ at temperatures lower than 1000°C from thermodynamic view-point. However, the rate of decomposition is very low and the practical system has not been proposed. In the patent⁽⁴⁶⁾, Nb or Ta metals or their compounds were reported to catalyze the decomposition of NOx at the temperatures of 300~800°C.

As for the catalyst for automotive exhaust gas, oxidation of CO, hydrocarbons and reduction of NO with a platinum metal catalyst of the perovskite type such as [K] [Nb_{0.9}Pt_{0.1}]O₃, [Sr] [Co_{0.7}Nb_{0.1}Ru_{0.2}]O₃ have been proposed.⁽⁴⁷⁾ The catalyst has the general formula ABO₃ in which 1~50% of the B cation sites are occupied by cations of Pt, Pd, or Rh, ≧5% of the B sites are occupied by each of 2 oxidation states of a variable valence metal such as Nb, V, Co etc. and the remaining B cation sites are occupied by Al ions.⁽⁴⁷⁾

The catalyst which consists of yttrium oxide, niobium oxide, lanthanum oxide, cerium oxide and iron oxide mixed with MnO₂ was also proposed for the automotive system.⁽⁴⁸⁾ However, MnO₂ is not recommended for use in such a system now.

8 - The Catalyst Electrode for Fuel Cell

A fuel cell is a primary battery wherein electrical energy is generated directly from the chemical energy of a combustible fuel by electrochemical reaction. Each fuel cell electrode comprises a conductor for the transport of the electrical energy generated in the cell in association with a catalyst for the half-cell reaction taking place at the particular electrode. Different catalysts are employed at each of the two electrodes in a given cell, since the half-cell reaction taking place at the oxygen electrode differs from the half-cell reaction taking

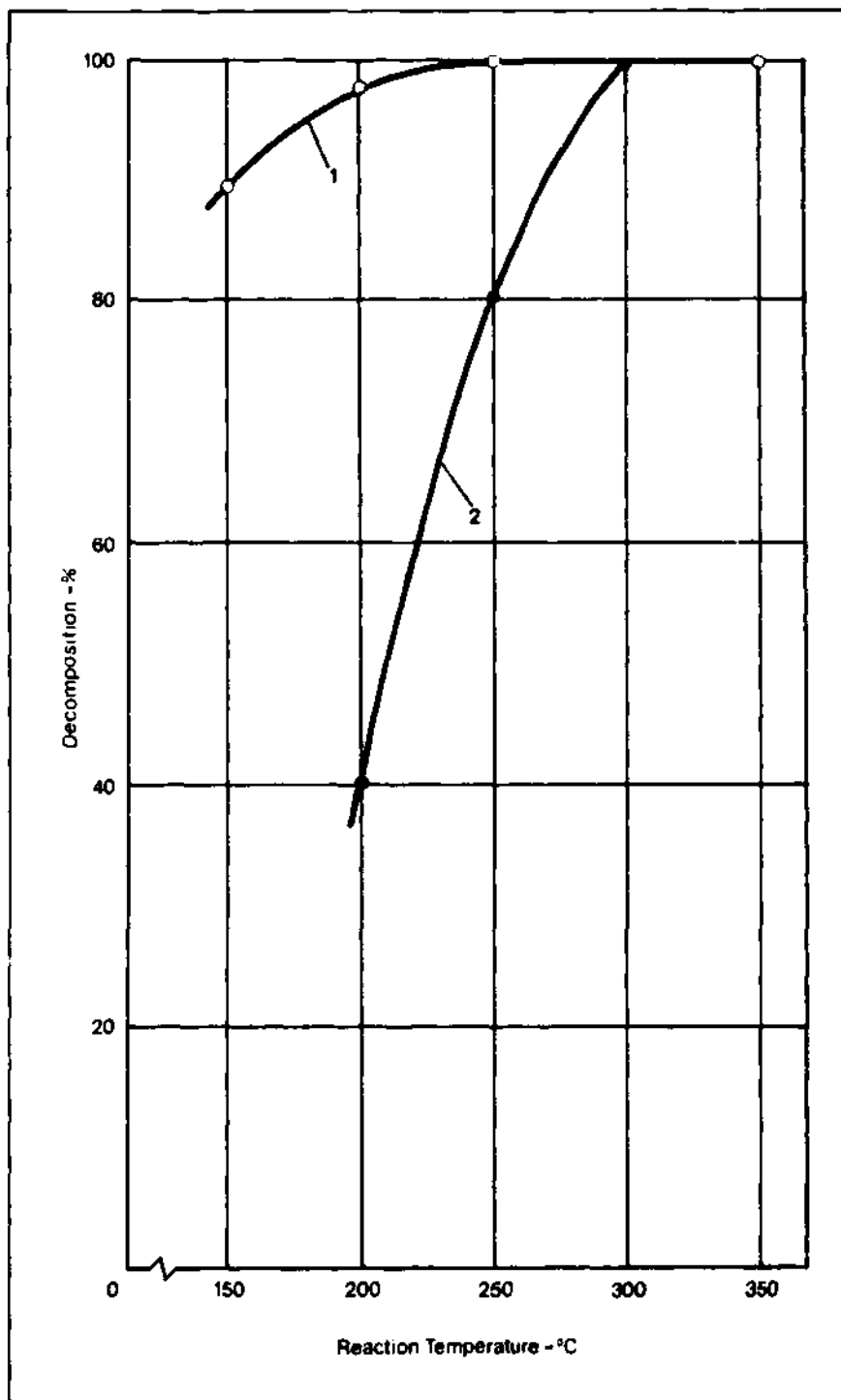


Fig 1 - Reduction of NOx with NH₃. 1. TiO₂-V₂O₅(5%)-Nb₂O₅(2.7%), 2. TiO₂-V₂O₅(7.5%)

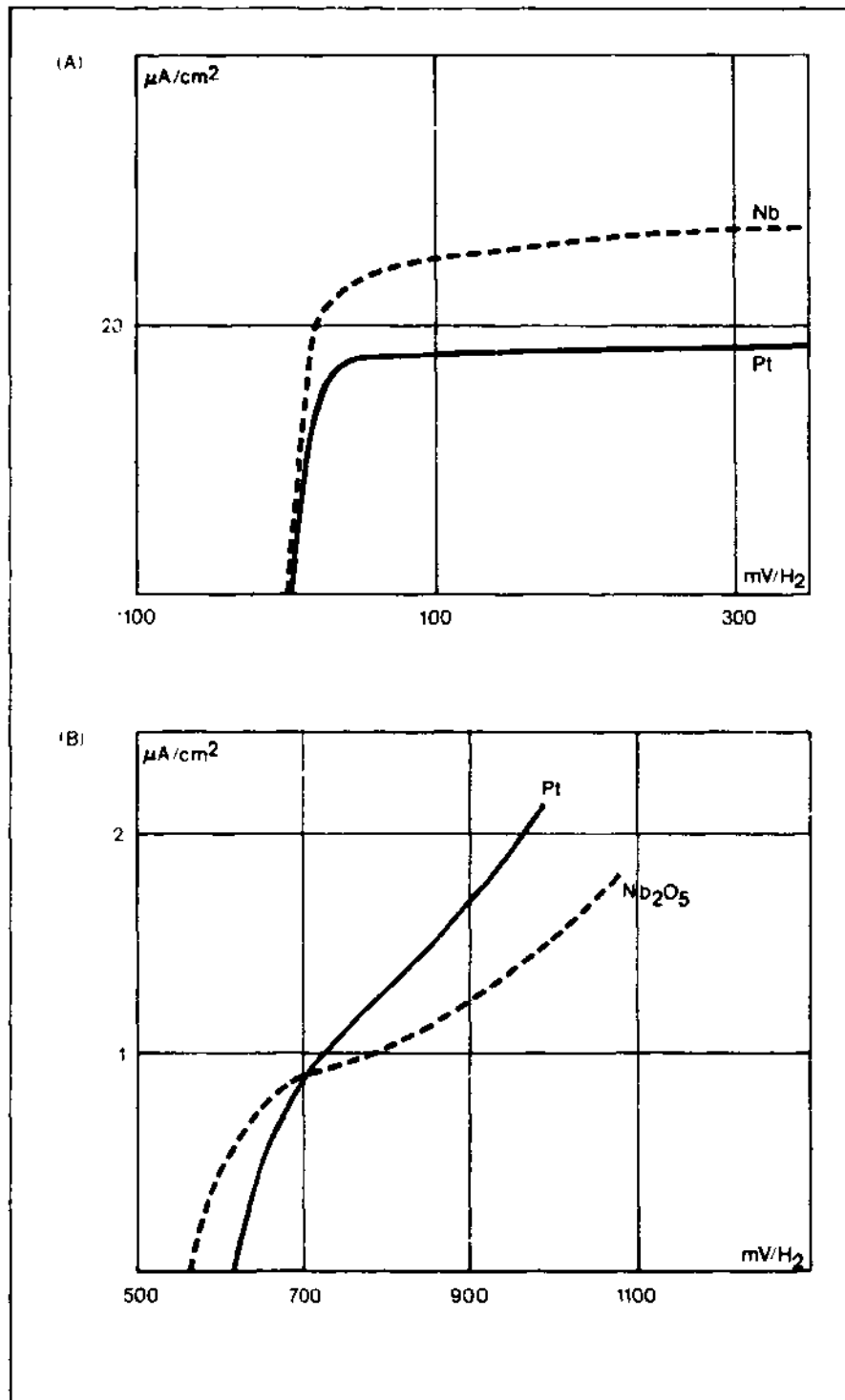


Fig. 2 - Current-potential curves. (A) H₂-O₂ fuel cell, (B) C₂H₄-O₂ fuel cell

place at the fuel electrode. Thus, the electrode should be conductive, corrosion resistant at high anodic electrode potentials in aqueous solution and good catalyst for the oxygen reduction reaction. The strontium niobium bronze of the formula Sr_xNbO_3 and barium tantalum bronze of the formula $\text{Ba}_{1-x}\text{TaO}_3$ were proposed for that purpose. ⁽⁴⁹⁾ Those bronzes may be utilized as such or in conjunction with a suitable conductive substrate, e.g., porous carbon, metals, etc. Strontium niobium bronze of the composition Sr_xNbO_3 , wherein x is a value between 0.70 and 0.95, were prepared. The powders were pressed into the form of an electrode, in admixture with nickel powder in a 1 to 2 volume ratio. The resultant electrode was tested as oxygen electrode in 1N NaOH supplied with gaseous oxygen at a pressure of 1 atm. The logarithm of the current density obtained was linear with potential exhibiting a slope of 60 mV and an exchange current density of about 10^{-9} amps/cm².

In an acidic electrolyte, Pt-Ti, Pt-Co, Pt-Nb alloys were used instead of Pt electrode by using H_2 , CH_4 , C_4H_{10} , C_5H_{12} , C_3H_8 , C_2H_6 , C_8H_{18} etc. as a fuel. ^(50,51) The alloy electrodes of Nb-Pt showed excellent activity compared to Pt black electrode as shown in Table 11.

As an anode of the fuel cell, Pt electrode is widely known as mentioned previously. In a French patent ⁽⁵²⁾, Nb metal or Nb oxide was used instead of Pt electrode. Pure niobium electrode showed a little bit higher activity than Pt in $\text{H}_2\text{-O}_2$ fuel cell as shown in Fig. 2(A). If the fuel contains carbon such as ethane or ethylene, the electrode of niobium oxide is suitable for the purpose as shown in Fig. 2(B).

In the other patents, an intermetallic compound of nickel and niobium, ⁽⁵³⁾ $\text{Nb}_2\text{O}_5\text{-TiO}_2$, ⁽⁵⁴⁾ platinum deposited on an alloy of Ru and Nb, ⁽⁵⁵⁾ W-Nb carbide ⁽⁵⁶⁾ are also reported to be effective for the electrode of the fuel cell.

9 - Hydrocarbon Synthesis from CO and H_2

The finite supply of natural liquid fuels has prompted a new interest in the synthesis of fuels from coal. A well known process in this regard is the Fischer-Tropsch synthesis of hydrocarbons from hydrogen and oxides of carbon. For the production of gaseous fuel from $\text{CO} + \text{H}_2$, many catalyst systems have been proposed until now. Among them, Ni supported on Nb_2O_5 or Ta_2O_5 was reported for the enhanced synthesis of paraffinic hydrocarbons with chain lengths from 2 to 6 carbon atoms. ⁽⁵⁷⁾ Niobium oxide supported Ni catalyst showed considerably higher activity compared to a conventional Ni/ Al_2O_3 catalyst as shown in Fig. 3 and higher selectivity for higher hydrocarbons as seen in Table 12. A catalyst of Ru/ Nb_2O_5 ⁽⁵⁸⁾ was

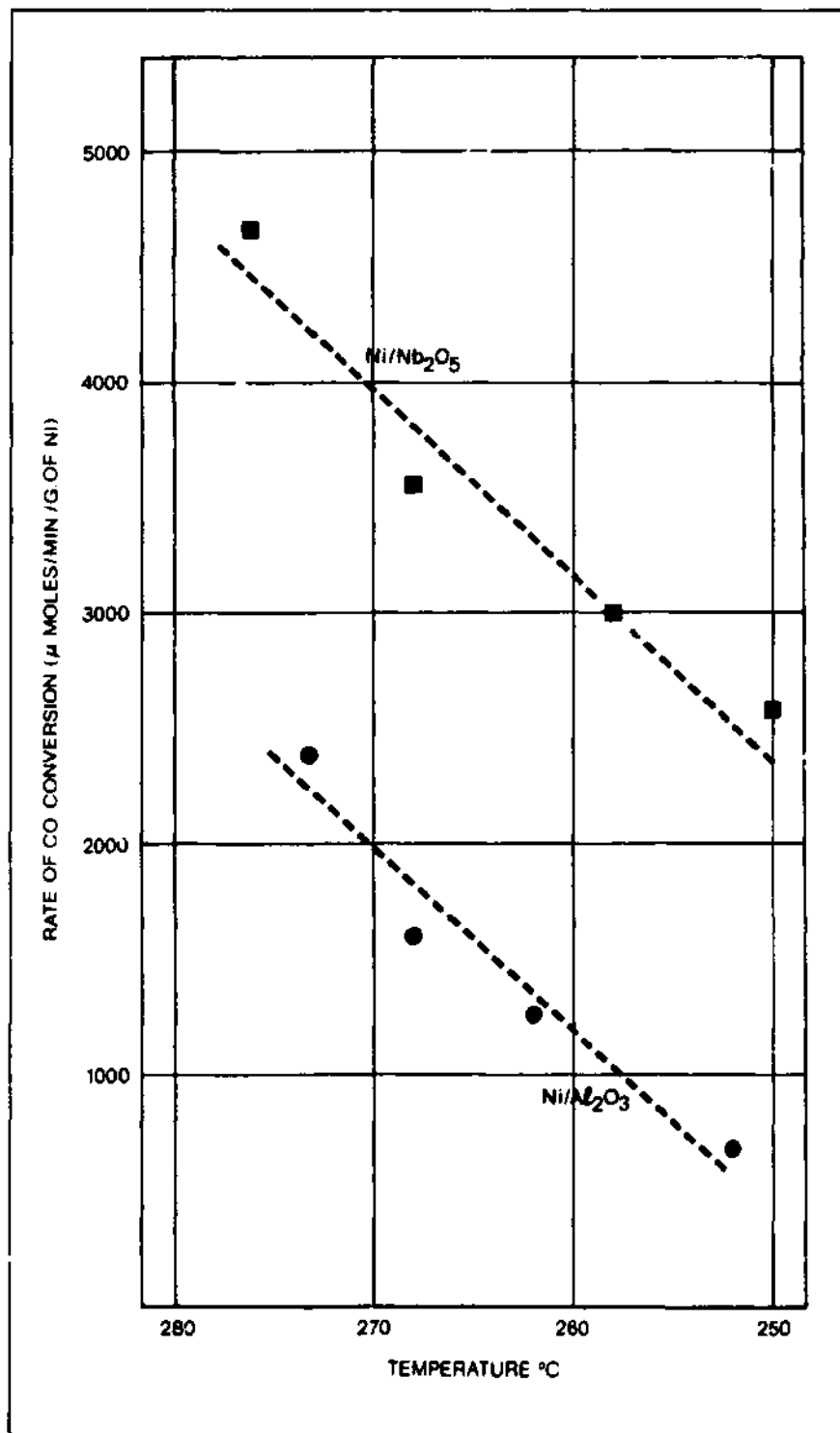


Fig 3 - Activity of nickel catalysts

also proposed to produce the higher hydrocarbons selectively. The data are shown in Table 13. Niobium oxide is known to show strong metal support interaction (SMSI) proposed by Exxon group,^(59, 60) which modifies the property of metal component on the catalyst. As seen in Fig. 4, the adsorbed amount of hydrogen chemisorption on Ir/Nb₂O₅ catalyst was drastically decreased when it was reduced at high temperatures. From the point of view mentioned before, the interaction of Nb₂O₅ support and metal component in the CO + H₂ reaction will be very interesting and important to prepare highly active and selective catalyst.

10 - Hydrogenation

1-Hexene, 1-heptene, and cyclohexene were reported to be hydrogenated with hydrogen over nickel hydride supported on SiO₂ to form 100% of hexane, heptane, and cyclohexane, respectively, at 160, 150 and 100°C.⁽⁶¹⁾ The NbNi₆Co hydrogenates n-hexane to form n-hexane at 145°C and the activity which is decreased by thiophene can be reactivated with hydrogen. The activity and the degree of reactivation are higher than British Petroleum catalyst and Ni₃Co.⁽⁶²⁾ The hydrogenation of benzene to cyclohexane was found to be catalysed with Ni-Nb in liquid phase, the activity being high compared to Ni or Ni-Ti as shown in Table 14.⁽⁶³⁾ The Ni-Nb catalyst is also active for the production of polyhydric alcohols by the hydrogenation of glucose and xylose at 115-120°C, 20-50 atm H₂.⁽⁶⁴⁾ Benzaldehyde is easily reduced with ethyl alcohol to form benzyl alcohol at 20°C over Ni-Nb (5%), the reaction rate is 8 times higher than that over a simple Ni catalyst.⁽⁶⁵⁾

11 - Oxidation

Acrolein, methacrolein, acrylic acid, methacrylic acid, maleic acid anhydride, phthalic acid, anthraquinone which are produced by oxidation reaction are important materials in chemical industry. Acrolein is used for manufacturing allyl alcohol, pyridine, 3-picoline, acrylic acid, acrylonitril, an DL-methionine. Acrylic acid is an important monomer for manufacturing homopolymer and copolymer which are widely used as paint material, adhesive agent, material to improve paper and textile, and finishing material of leather. Methacrylic acid is important for manufacturing methacryl acid methyl ester which is a monomer of acrylic glass. Maleic acid anhydride is used for improving unsaturated polyester resin and for manufacturing phthalic acid esters which are used as a plasticizer. Anthraquinone is an important intermediate in dye synthesis and is used also for production of hydrogen peroxide.

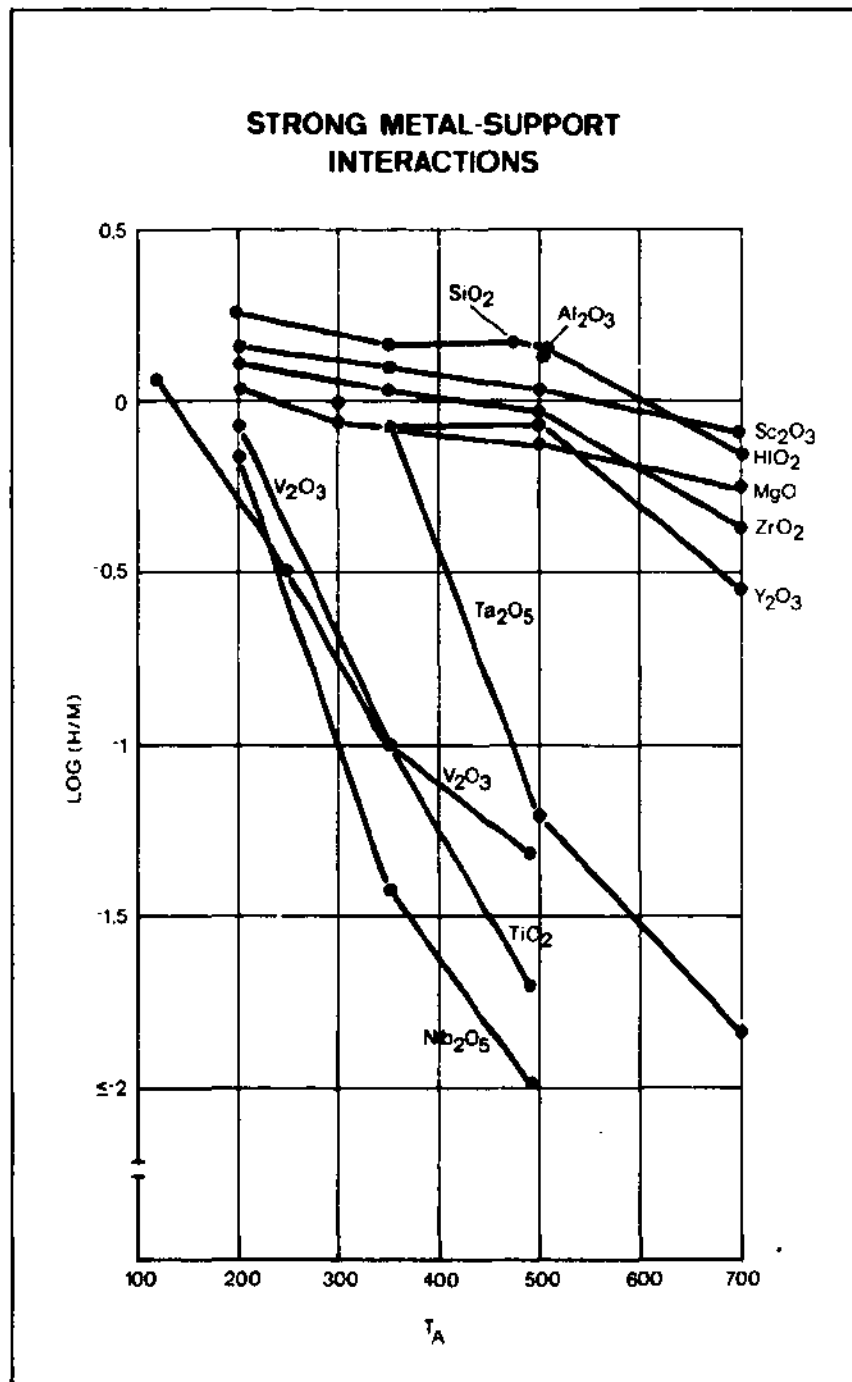


Fig. 4 · H₂ chemisorption vs temperature of activation for supported-iridium catalysts. H/M = atoms hydrogen adsorbed at 25°C per atom iridium present in catalyst; T = temperature of activation in hydrogen; wt% iridium = 1 for SiO₂, Al₂O₃, V₂O₃, and HfO₂ and 2 for all other catalysts.

11.1 - Acrolein and methacrolein

Acrolein is obtained by the oxidation of propylene with air. When $\text{FeSb}_{5.63}\text{O}_{11.1}/\text{SiO}_2$ is used as a catalyst, the conversion is 28% at 471°C. However, the addition of 7.2% Nb to the catalyst causes to increase the conversion to 38% under the same reaction condition. ⁽⁶⁶⁾ A complex oxide, $\text{Nb}_{0.2}\text{W}_{0.5}\text{Co}_5\text{Bi}_1\text{Fe}_{0.4}\text{Mo}_{12}\text{K}_{0.06}\text{Si}_{1.35}$, was found to be also active for the oxidation of propylene with air in the presence of water vapor at 315°C. The conversion of propylene was 98.5% and the selectivity for acrolein formation was 46.1%, the other product being acrylic acid. ⁽⁶⁷⁾

Methacrolein is obtained by the oxidation of isobutene with air over the catalysts containing Nb. The $\text{Mo}_{12}\text{Bi}_9\text{Nb}_1\text{Te}_1$ catalyst was most active for the oxidation, the conversion of isobutene and the selectivity being 88.3 and 83.6%, respectively, at 460°C. ⁽⁶⁸⁾ The $\text{Mo}_{12}\text{Nb}_1\text{Sb}_1\text{Te}_2\text{O}_{10-17}/\text{SiO}_2$ is reported to give 95.5% of conversion of isobutene and 73% of the selectivity for the formation of methacrolein together with methacrylic acid at 375-415°C. ^(69,70)

11.2 - Acrylic acid and methacrylic acid

Acrylic acid is easily obtained by the oxidation of acrolein with air over the catalysts containing Nb. With a $\text{Mo}_{12}\text{V}_3\text{Nb}_2\text{Fe}_1\text{Si}_{2.5}$ catalyst, the conversion of acrolein was more than 90% and the selectivity for the formation of acrylic acid was 91.8% at 210°C. ⁽⁷¹⁾ In the case of a $\text{Mo}_{10}\text{Nb}_7\text{Fe}_1\text{Cu}_1\text{Si}_{12.5}/\alpha\text{-Al}_2\text{O}_3$ catalyst, the conversion and the selectivity were 96.6 and 93.8%, respectively, at 250°C. ⁽⁷²⁾ The $\text{MoO}_3\text{-Nb}_2\text{O}_5/\text{SiO}_2$ catalyst gives 81% of acrylic acid at 417°C, the conversion of acrolein being 77.3%. ^(73,74) According to German patent, the conversion was 97.6% and the selectivity of acrylic acid was 92.6% at 305°C when $\text{Mo}_{2.4}\text{V}_{0.3}\text{Nb}_{0.3}\text{Fe}_{0.03}\text{Cu}_{0.03}\text{Co}_{0.03}\text{Cr}_{0.03}\text{Mn}_{0.03}/\text{SiO}_2\text{-Al}_2\text{O}_3$ was used as a catalyst. Acrylic acid is also obtained directly by oxidation of propylene with air. The selectivity of acrylic acid was 63.1% at 400°C over $\text{MoO}_3\text{-Nb}_2\text{O}_5\text{-As}_2\text{O}_3/\text{TiO}_2$, the other products being acetic acid and acrolein. ^(76,77) According to a Japan patent, the conversion of propylene and the selectivity of acrylic acid are 99.6 and 73.7% at 325°C with $\text{Nb}_{0.2}\text{W}_{0.5}\text{Co}_5\text{Bi}_1\text{Fe}_{0.4}\text{Mo}_{12}\text{K}_{0.06}\text{Si}_{1.35}$. ⁽⁶⁷⁾

Methacrylic acid is produced by the oxidation of methacrolein with air in the presence of water vapor over the catalysts containing Nb as shown in Table 15. ⁽⁷⁸⁻⁸³⁾ It is seen from the Table that $\text{Mo}_{12}\text{P}_2\text{Nb}_{2.4}\text{Cs}_2\text{Ti}_{0.1}\text{O}_{48.1}$ (No. 4) and $\text{Tl}_2\text{Mo}_{12}\text{In}_1\text{Sn}_1\text{P}_1\text{O}_{44}$ (No. 7) show high activity as well as high selectivity and $\text{Mo}_{12}\text{P}_2\text{Nb}_{2.4}\text{K}_2\text{O}_{48}$ (No. 5) shows the highest selectivity, though the activity is not so high. The $\text{Mo}_{12}\text{P}_1\text{Nb}_1\text{Cs}_{0.2}$ catalyst is reported to exhibit 84.1% of conversion and 91.0% of the selectivity for methacrylic

halogenation of hydrocarbons as shown in Table 16. Niobium fluoride⁽⁹⁵⁾ is also used for the decomposition of hydrocarbons deposited on the deactivated Friedel-Crafts type catalysts to reactivate it.

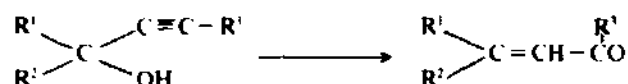
Niobium carbide is used as a catalyst of the synthesis of diamond from carbon.^(96, 97) Most effective catalyst has the composition of 50% NbC and 50% Cu as shown in Table 17.

For the production of heat resistant materials with large surface area⁽⁹⁸⁾, niobium carbide, boride or nitride was mixed with aluminum, silver, copper, cobalt, nickel or iron and heated at 1200°C~2000°C, then the metal components were dissolved by hot acid. The surface area of produced material is almost 10~50 m²/g.

Niobium metal supported on mordenite or acid clay was used as a catalyst for the disproportionation of toluene to produce benzene and xylene and for the trans alkylation of toluene and trimethyl benzene to produce xylene.⁽⁹⁹⁾ However the effect of Nb for the reaction was not clearly elucidated.

For the production of benzene from acetylene, Nb₂O₅ supported on Al₂O₃-SiO₂, ZrO₂-SiO₂ or SiO₂ was found to be highly active compared to other transition metal oxides⁽¹⁰⁰⁾ as shown in Table 18.

β-Acetylenic alcohols are isomerized to ethylenic carbonyl compounds by heating with a catalyst of NbCl₅.⁽¹⁰¹⁾



A mixture of 8.8 g of dehydrolinalool, 0.428 g of catalyst containing 48 mg of niobium and 40 cm³ of Vaseline oil is heated for 3 hrs at 140°C in a dry atmosphere. After distillation, citral is obtained with a degree of conversion of 70.6% and in a yield of 5.9% based on the dehydrolinalool converted.

Niobium catalysts (chloride, sulfate, phosphate, acetate ethoxide etc.) are known to catalyse the rearrangement of allyl alcohol⁽¹⁰²⁾ as well as other transition metal compounds such as V, W, Ta, Mo. A super acid, NbF₅ + HF, catalyses the reaction of toluene at 200°C to form benzene, ethylbenzene, xylenes, and cumene.⁽¹⁰³⁾

Nickel-niobium metal catalyst was used for the hydrogenolysis of maleic acid anhydrid to 1,4 butane diol and tetrahydrofurane⁽¹⁰⁴⁾ as well as Ni, Mo, W, Zr metals.

Niobium naphthalate was reported to catalyze the epoxidation of propylene with t-butylperoxide etc.^(105, 106, 107)

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Table 1
 OXYDEHYDROGENATION OF ETHANE
 Activity and Selectivity of Molybdenum Catalysts

Mixed oxide compositions	Temperature (°C) for initial activity, T_0	Selectivity (%) to C_2H_4 at T_0	Temperature (°C) for 10% conversion, T_{10}	Selectivity (%) to C_2H_4 at T_{10}
$Mo_{0.73}V_{0.18}Nb_{0.09}$	215	100	286	100
$Mo_{0.70}V_{0.17}Ti_{0.09}Mn_{0.04}$	215	100	295	100
$Mo_{0.69}V_{0.17}Ta_{0.06}Fe_{0.03}Si_{0.04}$	220	100	289	100
$Mo_{0.73}V_{0.18}Nb_{0.045}Mn_{0.045}$	243	100	300	100
$Mo_{0.63}V_{0.16}W_{0.06}Mn_{0.14}$	<255	100	295	100
$Mo_{0.70}V_{0.17}Ti_{0.06}Nb_{0.03}Mn_{0.04}$	260	84	400	80
$Mo_{0.70}V_{0.17}Nb_{0.06}Cu_{0.045}$	260	95	330	78
$Mo_{0.70}V_{0.17}Ta_{0.06}Mn_{0.045}$	309	85	385	63
$Mo_{0.70}V_{0.17}Ta_{0.06}Fe_{0.045}$	310	100	418	97
$Mo_{0.5}Mn_{0.5}$	320	100	550-600	35
$Mo_{0.63}Nb_{0.16}W_{0.06}Mn_{0.14}$	328	~100	400	10
$Mo_{0.70}V_{0.19}Fe_{0.03}$	370	100	435	87
$Mo_{0.75}W_{0.25}$	388	100	650	78
$Mo_{0.6}Ti_{0.4}$	390	100	600	65
$Mo_{0.73}Nb_{0.16}W_{0.09}$	~400	—	524	67
$Mo_{1.0}$	418	100	500	88
$Mo_{0.62}V_{0.06}$	444	~100	562	59
$Mo_{0.67}Bi_{0.03}Ti_{0.03}Mn_{0.11}Si_{0.11}$	460	100	505	100
$Mo_{0.75}W_{0.16}Pb_{0.9}$	474	>80	588	72
$Mo_{0.6}V_{0.4}$	500	100	540	100
$Mo_{0.67}V_{0.17}Mn_{0.17}$	502	100	505	100
$Mo_{0.6}Nb_{0.4}$	516	100	634	74

Table 2.
Oxidative dehydrogenation and dehydrogenation of hydrocarbons.

Catalyst	Reaction	Reaction temp. (°C)	Conversion (%)	Selectivity % to styrene	Ref.
1.0WO ₃ - 0.6Nb ₂ O ₅	ethylbenzene + O ₂	675	47	84	2)
"	(Cap.V.0.7 ~ 1.0V/hr/V)	700	56	83	2)
1.0WO ₃ - 1.0Nb ₂ O ₅	"	675	43	83	2)
"	"	700	54	83	2)
1.0Cr ₂ O ₃ - 2.0Nb ₂ O ₅	"	700	58	84	2)
1.0Cr ₂ O ₃ - 0.6Nb ₂ O ₅	"	700	63	82~85	2)
1.0Cr ₂ O ₃ - 1.0Nb ₂ O ₅ - 0.2K ₂ O	"	700	83	59.8	2)
"	"	650	67	89.9	2)
1.0Cr ₂ O ₃ - 4Nb ₂ O ₅ - 0.15K ₂ O	ethylpyridine + O ₂	625	51	81	2)
			(to vinyl pyridine)		
NbCx(C:46 atomic %)	ethylbenzene (3cm ³ /min)	600	11		4)
TcCx(C:42 ")	"	"	7		4)
ZrCx(C:48 ")	"	"	20		4)
Nb ₂ O ₅ /Alundum	isobutane + O ₂	450	isobutene was obtained		5)
	butane/steam/oxygen = 1/16/0.85				
	HC1/butane = 0.115				
	2-methyl butene-2 + O ₂	450	isobutene was obtained		5)
Nb ₂ O ₅	2-butene + O ₂ + HBr	700	85	65	6)
Nb ₂ O ₅ + 5% LiCl	"	700	84	75	6)
70% Al ₂ O ₃ - 30% Cr ₂ O ₃	n-heptane	537*		71**	7)
" + 5% K ₂ O	"	510*		85**	7)
70% Al ₂ O ₃ - 27.5% Cr ₂ O ₃ - 2.5% Nb ₂ O ₅	"	453*		64**	7)
" + 5% K ₂ O	"	461*		76**	7)
" + 5% CaO	"	455*		75**	7)
" + 5% SrO	"	448*		83**	7)

*) Temperature for 25% conversion **) Selectivity % to toluene

Table 3.
Ammoxidation of Hydrocarbons

Catalyst	Reaction	Reaction temp. (°C)	Conversion %		Ref.
			terephthalonitrile	p-toluenitrile	
TiO ₂ :V ₂ O ₅ =(97.9:2.1)– P ₂ O ₅ (0.49wt%)K ₂ O(0.146%)Nb ₂ O ₅ (0.244%)	p-xylene + NH ₃ + air (0.6) (4.8) (94.6)	385	80.1	3.2	8)
	"	395	84.5	1.5	8)
TiO ₂ –V ₂ O ₅ /SiO ₂ Na _x V ₂ O ₅ –Nb ₂ O ₅ /α–Al ₂ O ₃ (X=0–1, V ₂ O ₅ :8.5%, Nb ₂ O ₅ :0.6%)	"	395	65.3	3.3	8)
	p-xylene + NH ₃ + O ₂ 1 : 3.2 : 3.0	430	65.0	25.2	9, 10)
"	p-xylene + NH ₃ + O ₂ 1 : 3.2 : 6.0	430	72.5	8.3	9, 10)
MoO ₃ –Nb ₂ O ₅ –P ₂ O ₅ /SiO ₂ (11.9) (3.01) (4.9)	propane + NH ₃ + air	485	propane 33	acrylonitrile 24	11)
	"	485	44	54	11)
WO ₃ –CuO–Nb ₂ O ₅	isobutene + NH ₃ + air + H ₂ O		methacrylic acid nitrile 43		12)
	propylene + NO + N ₂	435	acrylonitrile 85		12)
Bi ₂ O ₃ –Nb ₂ O ₅ –P ₂ O ₅ –NiO (2) (1) (1) (2)	"	435	82		12)
Bi ₂ O ₃ –TiO ₂	"	490	76		12)

Table 4
Synthesis of Alkylpyridines at 450°C

Catalyst	Reaction	2-Picoline	Products (%) 4-Picoline	Other Pyridines
SiO ₂ -Al ₂ O ₃	Acetaldehyde +			
	NO	15.5	14.1	10.1
SiO ₂ -Al ₂ O ₃ + Nb ₂ O ₅ (10 wt%)	"	20.2	18.5	13
SiO ₂ -Al ₂ O ₃ + Sb ₂ O ₃ + K ₂ O	"	31.9	26.3	9.7

Table 5
Reforming of naphtha
(aromatics 9 wt%, naphthen 29 wt%, paraffin 62 wt%)

Catalyst	Reaction temp. (°C)	Pressure (bars)	Octane Value	Ref.
Pt, Ir, Nb, Cl/Al ₂ O ₃	485	25	93	15)
(0.35%) (0.05%) (0.15%) (1.2%)	530	10	104	15)
Pt, Ir, Cl/Al ₂ O ₃	485	25	91.2	15)
	530	10	102.5	15)

n-Heptane reaction

Catalyst	Reaction temp. (°C)	Total conversion %	Conversion to aromatics %	Conversion of isomerization %	Ref.
Pt,Nb,F/Al ₂ O ₃	350	87	1	40	16)
Pr,Nb/Al ₂ O ₃	350	45	9	12	16)
Pr,Tu,F/Al ₂ O ₃	350	90	23	33	16)
Pt/Al ₂ O ₃	350	32	8	10	16)

Table 6
Polyester production reaction at 280°C

Catalyst	wt %	Time	Viscosity	Color of product
NbCl ₅	0.0070	—	0.63	yellow
Nb ₂ O ₅	0.0034	—	0.62	"
Hydrolyzed NbCl ₅	0.0046	—	0.64	white
Nb metal powder	0.02	4 (hr)	0.66	L=79.6 (clarity)
Sb ₂ O ₃	0.03	3	0.67	L=73.3 (clarity)
Niobium penta- phenoxide	0.056	40 (min)	0.88	—
Tungsten hexa- phenoxide	0.074	40 (min)	0.53	—

Table 7

Polymerization of 1,3-butadiene

Metal ion	Yield (%)	1,4-cis (%)	Metal ion	Yield (%)	1,4-cis (%)
Ti(IV)	35	38	Pd(II)	37	16
Cr(III)	32	46	Rh(III)	52	41
Nb(IV)	36	25	La(III)	39	24
Mn(III)	56	52	Ce(IV)	50.5	21
Ge(IV)	41	29	Tl(III)	40.5	20
Ta(IV)	38	33	Au(III)	54.5	25
Mo(V)	41.5	43	Th(IV)	46	22

Table 8

Polymerization of propylene (TiCl₄ + Triethyl Al + Metal halide)

Catalyst	Polymerization rate	Crystallinity of polymers (%)
NbCl ₅ /TiCl ₄ =0.017	28.9	98.3
BeCl ₂ /TiCl ₄ =0.017	29.1	98.6
MnCl ₂ /TiCl ₄ =0.017	33.4	98.3
GeCl ₄ /TiCl ₄ =0.017	33.3	98.3
RuCl ₃ /TiCl ₄ =0.017	36.8	97.4
TeCl ₄ /TiCl ₄ =0.017	28.2	98.9
TiCl ₄	30.4	92.8

Table 9

Conversion of hydrocarbons

Catalyst	Reactant	Reaction temp. (°C)	Products
[(L) _a (NO) _b McZd] _x M:Nb or V, Z:hydrogen L:Ligand	pentene	room temp.	butenes (1.7 wt%) + hexenes (2.1 wt%)
10% Nb ₂ O ₅ /SiO ₂	propylene	1000°F	C ₁ (2.1%), C ₂ (96.3%), 1-C ₃ (0.5%) i-C ₃ (0.5%), C-C ₄ (0.3%), C ₄ (0.3%) Selectivity to ethylene and butenes = 90%
NbF ₅ + HF + H ₂ (37.6g)(20g)(100psig.)	n-hexane + cyclo hexane	50°C (1 hr)	C ₁ (0.11), i-C ₂ (0.07) n-C ₂ (0.06), i-C ₃ + n-C ₃ (0.07) 2,2-dimethyl C ₄ (11.92) 2,3-dimethyl C ₄ + 2 methyl C ₄ (35.75) 3 methyl C ₄ (12.59), n-C ₄ (27.87) methylcyclo C ₄ (1.27) cyclo C ₄ (6.82) benzene (3.45)
Nb metal	n-hexane	186°C	C ₁ + C ₂ (40.2), C ₃ (18.7), i-C ₃ (0.2), n-C ₃ (20.3), i-C ₄ (0.4), n-C ₄ (19.0), C-C ₄ (1.2), i-C ₄ (trace)
	"	224°C	C ₁ + C ₂ (31.6), C ₃ (18.7), i-C ₃ (0.3), n-C ₃ (19.6), i-C ₄ (0.3), n-C ₄ (20.8), C-C ₄ (1.6), i-C ₄ (0.8), benzene (5.5), n-C ₄ (2.2)

Table 10

NO_x + NH₃ reaction NO:300 ppm, NH₃:450 ppm, SO₂:500 ppm, O₂:15%

Catalyst	Initial conv. (%)	After 15 hr. (%)	After 30 hr. (%)
TiO ₂ -V ₂ O ₅ -Nb ₂ O ₅	99	94	89
TiO ₂ -V ₂ O ₅	40	12	7

Table 11

Pt-Nb Electrode

Composition of anode catalyst	Potential in mV vs AgCl/Ag electrode at indicated current density in mA/cm ²					
	0	5	10	20	30	50
Alloy of 30% Nb-70% Pt	100	130	150	200	240	300
Pt alone	90	240	280	340	380	430

Table 12

Fischer-Tropsch Synthesis

Selectivity of Nickel Catalysis
(Reaction Conditions: H₂/CO = 3. Pressure = 103 kPa)

Catalyst	Temp. (°C)	% CO Conv.	Products (Wt. %)					
			C ₁	C ₂	C ₃	C ₄	C ₅	C ₆
1% Ni/Ta ₂ O ₅	275	11.1	58	17	14	7	4	trace
1% Ni/Nb ₂ O ₅	276	6.4	60	18	13	6	3	trace
1% Ni/Al ₂ O ₃	273	6.6	88	9	3	—	—	—
1% Ni/Ta ₂ O ₅	266	8.1	50	18	16	10	6	trace
1% Ni/Nb ₂ O ₅	268	4.9	54	20	15	7	4	trace
1% Ni/Al ₂ O ₃	268	4.5	87	11	2	—	—	—
1% Ni/Ta ₂ O ₅	257	6.6	45	19	17	12	8	trace
1% Ni/Nb ₂ O ₅ *	258	8.3	48	18	17	9	8	trace
1% Ni/Al ₂ O ₃	262	3.2	88	12	trace	—	—	—
1% Ni/Ta ₂ O ₅	249	3.4	40	20	17	16	7	trace
1% Ni/Nb ₂ O ₅ *	250	7.2	47	20	17	9	7	trace
1% Ni/Al ₂ O ₃	252	1.9	88	12	trace	—	—	—

All reactions were conducted at about 2400 hr⁻¹, except those with*, which were conducted at 1200 hr⁻¹.

Table 13.
Selectivity of several Ru catalysts
 (Reaction conditions: H₂/CO = 3; Pressure = 103 kPa)

Catalyst	Temperature (°C)	Conversion %CO	Obtained hydrocarbons (mol. %)									
			CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆ C ₃ H ₈	C ₄ H ₆ C ₄ H ₁₀	C ₅ H ₁₀ C ₅ H ₁₂	C ₆ ⁺	C ₂ -C ₅ Olefin	C ₂ ⁺	
Ru-Metal (c)	226	3.5	96	0	4	trace	0	0	0	0	0	4
4% Ru/Carbon (b)	243	2.5	98	0	2	trace	0	0	0	0	0	2
	234	1.6	98	0	2	0	0	0	0	0	0	2
1% Ru/SiO ₂ (a)	232	4.1	87	1/2	6 1/2	4	1	1	trace	2 1/2	13	
5% Ru/Si ₂ (a)	233	16.7	86	trace	7 1/2	4	1 1/2	1	trace	trace	14	
	228	8.8	6612.....		8 1/2	6	4 1/2	3	11	34	
1% Ru/Al ₂ O ₃ (a)	244	14.1	7111.....		7	5	4	2	10	29	
	239	13.6	67	1/2	10	6 1/2	8 1/2	4 1/2	3	—	33	
1% Ru/Nb ₂ O ₅ (a)	234	7.8	4811.....		12 1/2	9 1/2	7	12	22	52	
1% Ru/Nb ₂ O ₅ (a)	244	3.7	4114.....		18	11	11	5	27	59	

(a) Catalyst reduced 1 hour at 450°C prior to introducing starting material (CO + H₂).

(b) Catalyst reduced 1 hour at 400°C prior to introducing starting material.

(c) Catalyst reduced 1 hour at 300°C prior to introducing starting material.

C₆⁺ hydrocarbon with 6 or more carbon atoms.

C₂⁺ olefin hydrocarbon with 2 or more carbon atoms.

Table 14.
Hydrogenation of benzene at 160°C, 50 atm H₂

Catalyst	Cyclohexane (%)		
	20	40	60 min
Ni	20	39	61
Ni-Ti	23	45	68
Ni-Nb(1% Nb)	34	67	100

Table 15.
Production of methacrylic acid by oxidation of methacrolein

No.	Catalyst	Reaction temp. (°C)	Conversion (%)	Selectivity (%)		Ref.
				Methacrylic acid	Acetic acid	
1	Mo ₁₂ P ₂ Nb _{2.4} Cs ₂ O ₂₈	350	90.3	79.7	9.0	78)
2	Mo ₁₂ P ₂ Nb ₂ Cs ₂ O ₂₇	360	86.0	75.1	9.7	78)
3	Mo ₁₂ P ₁ Ta ₁ V ₁ Cs ₁ O ₁₄	360	81.2	70.3	16.6	78)
4	Mo ₁₂ P ₂ Nb _{2.4} Cs ₂ Tl _{0.1} O _{28.1}	368	90.1	81.2	4.0	78)
5	Mo ₁₂ P ₂ Nb _{2.4} K ₂ O ₂₈	340	71.4	91.2	5.0	78)
6	Tl ₂ Mo ₁₂ Nb ₁ Fe ₁ P ₁ O ₄₃	340	78	84	9	79)
7	Tl ₂ Mo ₁₂ In ₁ Sn ₁ P ₁ O ₄₄	340	95	81	7	79)
8	Tl ₂ Mo ₁₂ Zr ₁ Nb ₁ P ₁ O ₄₅	340	77	78	9	79)
9	Tl ₂ Mo ₁₂ Nb ₁ In ₁ P ₁ O ₄₄	340	97	68	6	79)
10	Mo ₁₂ P ₁ V ₁ O ₄₃	340	47	56	7	79)
11	Mo ₁₂ Nb ₁ P ₁	340	62	73.8	8.2	80)
12	Mo ₁₂ Bi ₁ Nb ₁ P ₁	340	82.5	75.6	7.3	80)
13	Mo ₁₂ P ₁ Nb ₁ Sb ₁	370	78.3	73.4		81)
14	Mo ₁₂ P ₁ Nb ₁ Cs _{0.2}	370	77.8	75.9		81)
15	Mo ₁₂ P ₁ Nb ₁ Tl _{0.2}	370	73.3	75.5		81)
16	Mo ₁₂ P ₂ Cs ₂ Bi _{0.5} Nb _{0.5}	405	75	65.1		82)
		405	75.1	65.0		82)
			(after 30 days)	(after 30 days)		
17	Mo ₁₂ P ₂ Cs ₂ Nb ₁ Mn ₁	330	81.6	81		83)
18	Mo ₁₂ P ₂ Cs ₁ Nb ₁ V ₁ Cu _{0.3}	330	82.6	83.2		83)

Table 16

Fluorination of benzotrichloride

Catalyst	% weight of catalyst	Temp. (°C)	Benzotri-fluoride	Products Benzodi-fluoride	Benzofluoro-dichloride
NbCl ₅	0.5	48-52	77.2	21.4	0.1
"	1.4	66-72	95.5	0.2	—
TaCl ₅	0.18	55-59	94.0	3.8	—
ReCl ₅	0.19	57-59	60.1	39.8	—

Production of perfluoroalkyl iodide from perfluoroalkene, iode and iode penta-fluoride

		Temp. (°C)	C ₂ F ₅ I yield (%)
Nb	0.10	75	97
NbF ₅	0.10	"	"
AlF ₃	0.10	"	66
CaF ₂	0.10	"	34

Table 17

Synthesis of diamond

Catalyst	Pressure (atm)	Temp. (°C)	Time (min)	Diamond produced (mg)
50%NbC-50%Cu	71,000	1,800	15	11.4
50%NbC-50%Ag	"	"	"	6.2
50%Nb-50%Cu	"	"	"	10.4
50%Nb-50%Ag	"	"	"	1.2
50%NbC-50%Au	"	"	"	5.8
50%Nb-50%Au	"	"	"	0.8
50%NbC-25%Ag-25%Cu	"	"	"	11.3

Table 18
Polymerization of Acetylene to Benzene

Active Component	Carrier	Maximum Reaction Temp. (°C)	Activity (G - C ₆ H ₆ /g catalyst)
CrO ₃	Al ₂ O ₃ - SiO ₂	90	8.3
		120	5.4
	ZrO ₂ - SiO ₂	110	5.1
	SiO ₂ , large-pored	120	5.5
	Al ₂ O ₃ - SiO ₂ + Sr ⁺⁺	85	8.3
	Al ₂ O ₃ - SiO ₂ , KAc treated	85	4.5
	Al ₂ O ₃ - SiO ₂ (Steam-treated at 250°C)	85	4.6
Nb ₂ O ₅	Al ₂ O ₃ - SiO ₂	170	7.8
	ZrO ₂ - SiO ₂	140	6.4
	SiO ₂ , large-pored	120	6.4
TaOF ₅	Al ₂ O ₃ - SiO ₂	200	5.3
V ₂ O ₅	Al ₂ O ₃ - SiO ₂	270	1.0
MoO ₃	Al ₂ O ₃ - SiO ₂	220	0.2
TiO ₂	Al ₂ O ₃ - SiO ₂	350	Trace
ZrO ₂	SiO ₂	~ 350	Nil