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Niobic acid — a new heterogeneous catalyst for processes in petrochemical and organic syntheses

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Abstract. Questions associated with the application of niobium compounds in catalysis are considered. Niobic acid $Nb_2O_5 \cdot nH_2O$ contains an appreciable amount of water, but its surface exhibits a high acidity — equivalent to the acidity of 70% sulfuric acid. This unusual solid acid manifests not only a high activity and sensitivity but also an appreciable stability as a catalyst in reactions in which water is present or is evolved (condensation, hydration, dehydration, and esterification). It may be used also as a catalyst in other reactions. The structure and properties of the surface of niobic acid are examined. The bibliography includes 54 references.

I. Introduction

Technologies which permit industrial production satisfying world standards, giving rise to a high output without contamination of the environment, have acquired prime importance at the present time. In this connection, the use of niobic acid, the term usually applied to hydrated niobium pentoxide $Nb_2O_5 \cdot nH_2O$, as a solid acid catalyst for a number of processes can undoubtedly be of practical interest. The most important property of niobic acid is that, after heat treatment at 100 – 300 °C, its surface acquires a high acidity, although an appreciable amount of water is present on it.[1] The activity of niobic acid is manifested already at a low temperature (100 – 120 °C) even in the presence of water vapour. The oxides of other metals do not possess similar properties: it is known that their acidity is lost or diminishes as a consequence of the adsorption of water. The use of niobic acid as a catalyst in reactions with participation or elimination of water — esterification, hydration, dehydration, Prins reaction, hydrolysis, and others — is especially effective. In these reactions, niobic acid exhibits a high activity, selectivity, and stability.[1 – 3] Even in the presence of components with a reducing capacity, the acidity of niobic acid does not diminish, since the oxide Nb_2O_5 is stable.

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Until recently, niobium catalysts have not attracted special attention despite the fact that catalysts based on molybdenum and vanadium — elements adjoining niobium in the Periodic System — have been widely used in industry. However, during approximately the last five years, the attitude to niobium-based catalysts and especially to niobic acid changed significantly.[1 – 3] Niobic acid has begun to be used in Japan as an industrial catalyst of condensation, dehydration, hydration, and esterification reactions.[2]

H_2SO_4, H_3PO_4, HF, and sulfonic acid cation-exchange resins are frequently used in industrial processes as acid catalysts. A number of problems associated with the corrosion of equipment, the inadequate selectivity of the processes, the presence of a large amount of waste, and the need to utilise the spent catalysts and their toxicity then arise. The employment of niobic acid could help in many instances to solve these problems. Not only hydrated niobium oxide (niobic acid) but all composite systems based on niobium oxide are of interest for catalysis. There are prospects for their employment as both catalysts and carriers.

The world niobium resources (excluding the Union of Independent States) amount to 28 000 tonnes, which exceeds somewhat the resources of elements such as molybdenum, tungsten, and cobalt.[5] According to data concerning the state of the world market in niobium and its consumption,[6] the production of niobium in 1987 was 14 900 tonnes, of which 85% was produced by the CBMM Company (Brazil). According to these data, 87% of niobium is consumed as an additive to steel, 10% in the preparation of nickel – niobium alloys, and the rest in the manufacture of optical glasses, dielectric materials, and superconductors. According to a forecast,[5] the world production of niobium will increase by 8% – 10% annually.

Niobium is also extracted in our country.[5] An appreciable amount of niobium is present in the waste from tungsten ore in the processing plants (niobium is known to accompany tungsten). A low-waste technology has been proposed for the extraction of a niobium and tantalum concentrate from such waste.[7] Instances of occupational poisoning by niobium have not been described.[8]

The principal results achieved as a result of the use of niobic acid and other niobium-based materials in catalysis have been described in reviews [1 – 3] and in the proceedings of an international symposium on catalysis by niobium materials.[4]

The aim of the present review is to survey the latest advances in catalysis by niobic acid and other niobium-based compounds and also to draw the attention of investigators to this new problem, which is promising from the practical standpoint.

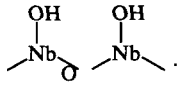
Data published during the last five years are mainly considered. References to earlier studies may be found in the papers of Tanabe[1,3] and Okazaki[2].

II. The structure and properties of the surface of niobic acid

Hydrated niobium pentoxide $Nb_2O_5 \cdot nH_2O$ is a white polymeric amorphous material. Its composition is variable owing to the inconstancy of its water content,[9] which varies depending on the method of preparation and drying. The nature and structure of niobic acid and of the products of its thermal decomposition have been examined in a number of publications.[9-11] It was established[9] that hydrated niobium pentoxide consists of the niobic isopolyacid having the composition $H_8Nb_6O_{19}$. On heating, the hydrated isopolyacid splits off water, forming stoichiometric hydrates, while above 1200 °C it also loses a certain amount of oxygen with formation of oxygen-deficient non-stoichiometric niobium oxides:[10]

$$H_8Nb_6O_{19} \cdot 18H_2O \longrightarrow H_8Nb_6O_{19} \cdot 12H_2O \longrightarrow$$
$$\longrightarrow H_8Nb_6O_{19} \cdot 6H_2O \longrightarrow H_8Nb_6O_{19} \cdot 3H_2O \longrightarrow$$
$$\longrightarrow H_8Nb_6O_{19} \longrightarrow [H_2Nb_6O_{16}]_n \xrightarrow{1200\ ^\circ C}$$
$$\longrightarrow [Nb_6O_{15}]_n \longrightarrow [NbO_{2.5-2.33}]_m .$$

The amorphous modification, called γ-niobic isopolyacid, exists up to 435 °C. On further heating, it passes to the low-temperature crystalline state and at 830 °C to the high-temperature crystalline state (α-Nb_2O_5). The steric structure of $H_8Nb_6O_{19}$, which will henceforth be referred to as niobic acid by tradition, is illustrated in Fig. 1. In this structure, the eight protons are located over the triangular faces of the octahedron formed by the six niobium atoms. Among the oxygen atoms, 12 bridging atoms, 6 terminal atoms, and one central atom are distinguished. Each hydrogen atom is coordinated to three bridging oxygen atoms, three terminal oxygen atoms, and one central oxygen atom. The protons in niobic acid form part of the composition of the hydroxy-groups linked to the niobium atoms:



The H...H distance is fairly long—more than 4 Å. Conductimetric and IR spectroscopic studies suggested the possibility of the migration of protons in the niobic acid matrix.[9] Water molecules are linked to $H_8Nb_6O_{19}$ by a hydrogen bond via the peripheral oxygen atoms.[10] Only 1.2% of the protons in $H_8Nb_6O_{19}$ can be substituted by sodium ions in a slow exchange process.[9]

When $Nb_2O_5 \cdot nH_2O$ is heated, the derivatogram shows[12] two endothermic peaks at 90 and 190 °C. The weight loss at these temperatures is associated with the dehydration of the gel-like niobic acid and its transition to the amorphous state. The surface of niobic acid then acquires strong acidic properties ($H_0 \leqslant -5.6$), corresponding to the acidity of 70% sulfuric acid. Strong acid centres arise even after mild heat treatment of niobic acid at 100 °C and the residual water can then cover the entire surface of the catalyst. The acidity of metal oxides is usually lost or reduced as a result of the adsorption of water. For example, strong acid centres appear on the surfaces of the $SiO_2-Al_2O_3$ and SiO_2-TiO_2 systems only after heat treatment at about 500 °C simultaneously with the removal of water from the surface. The dehydration of $Nb_2O_5 \cdot nH_2O$ terminates at 300 °C. Further heating from 300 to 700 °C is not accompanied by a change in the weight of the specimen. After heat treatment at 500 °C, niobic acid becomes almost inactive and does not exhibit any acid properties.[1,12] This occurs as a consequence of the phase transition of the amorphous $Nb_2O_5 \cdot nH_2O$ to a crystalline phase.[1]

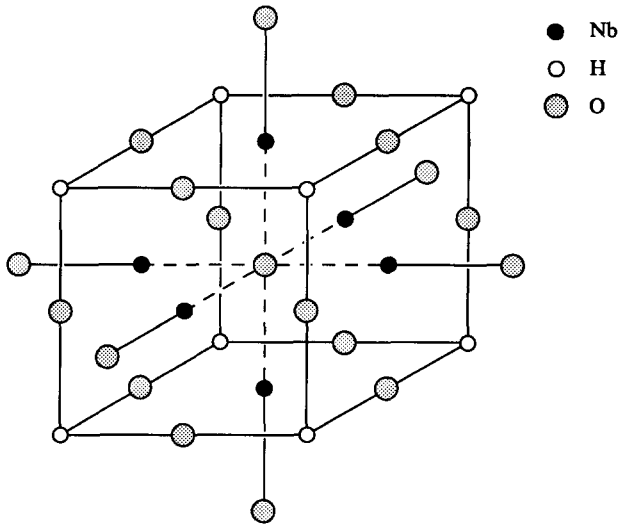


Figure 1. The structure of $H_8Nb_6O_{19}$.

According to Tanabe,[1] the specific surface of niobic acid is respectively 164, 126, and 42 $m^2\ g^{-1}$ after evacuation at 100, 300, and 500 °C. The number of OH groups on the surface of niobic acid depends on the heat treatment temperature:[1,12]

T/°C	120	200	300	400
[OH]/mmol g^{-1}	1.0	0.8	0.7	0.55

The acid properties of niobic acid, investigated by titration with *n*-butylamine in the presence of Hammett indicators, can be inferred from Fig. 2. The greatest number of strong acid centres ($H_0 = -5.6$) are present in niobic acid after its heat treatment at 120–300 °C.

Analysis of the IR spectra of pyridine adsorbed on niobic acid shows that the intensity of the absorption band (a. b.) corresponding to the Brønsted acid is a maximum when the temperature of the preliminary heat treatment of the specimen is 100 °C (Fig. 3*a*). It diminishes with increase in the heat treatment temperature.[12] On the other hand, the

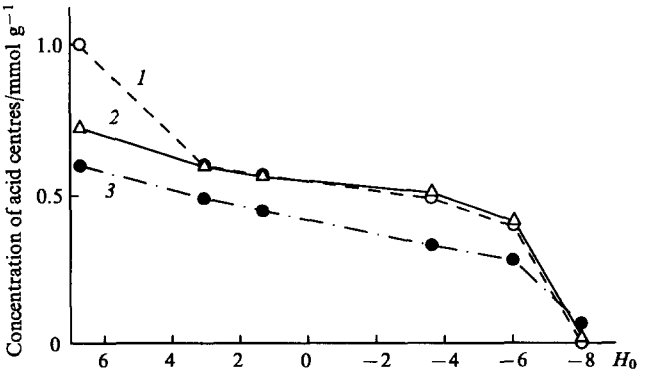


Figure 2. Distribution of the acid centres of niobic acid with respect to their strength as a function of the heat treatment temperature (°C): *1*, 120; *2*, 200; *3*, 300.[1]

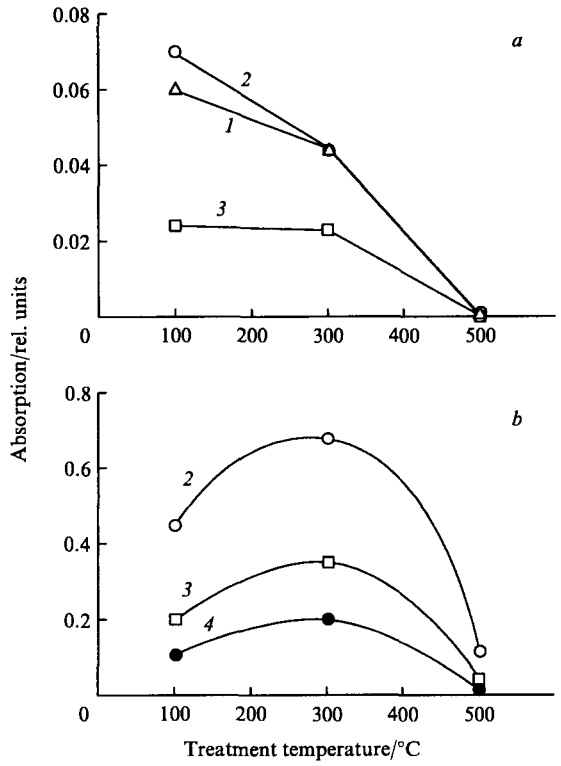


Figure 3. Variation of the Brønsted (*a*) and Lewis (*b*) acidities of niobic acid with the temperature of the preliminary treatment with the specimen evacuated after the adsorption of pyridine. Treatment temperature (°C): *1*, room temperature; *2*, 100; *3*, 200; *4*, 300.

intensity of the spectral band corresponding to the Lewis acid reaches a maximum at a preliminary heat treatment temperature of 300 °C (Fig. 3*b*).

The study of the IR spectra of adsorbed CO_2 showed that niobic acid has only weak basic properties.[12]

The data presented in Table 1 make it possible to compare the properties of the surfaces of different oxides.[2]

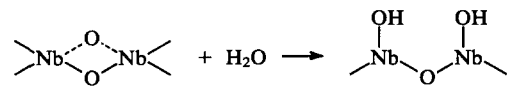
Table 1. The properties of the surfaces of different oxides treated with steam at 300 °C for 3 h.

Oxide	Specific surface/$m^2\ g^{-1}$	OH groups on the surface/mmol g^{-1}	OH groups on 100 Å^2
Nb_2O_5	124	0.84	4.2
Al_2O_3	218	2.29	6.3
TiO_2	177	1.14	3.9
ZrO_2	234	1.43	3.7

In terms of the density of OH groups, niobic acid does not differ from other oxides, but its specific surface is smaller.

The formation of highly acid centres on the surface of niobic acid cannot be explained solely by its structure. The elucidation of this problem would help in the development of new types of solid acid materials.[1]

It was of interest that the acidity of niobic acid evacuated at 300 and 400 °C virtually returns to the initial value after its treatment with water vapour for 3 h and subsequent evacuation at 100 °C, while the number of OH groups on the surface increases.[1,2] This finding is explained by the fact that, on heating to 400 °C, the process involving the removal of OH groups from the surface is almost completed and the acid passes to an unstable state in which crystallisation does not yet begin.



In this state, there is a possibility of hydration by water vapour.[2]

Even in the presence of components with a reducing capacity, the acidity of niobic acid does not fall,[1] since the oxide Nb_2O_5 is stable and is reduced with difficulty, in contrast to the related oxides V_2O_5 and MoO_3. Niobium pentoxide is reduced by hydrogen only at 800–1350 °C.

Niobic acid contains Fe, Cl, Na, and K as impurities. With decrease in their amount to several parts per million, very strong acid centres ($H_0 \leqslant -8.2$) are observed in niobic acid and are retained even in the presence of water vapour.[2] This phenomenon is of interest from the practical point of view.

It has also been noted[13] that, on promotion with 1 M phosphoric acid, the crystallisation of niobic acid begins at 570 °C and not at 435 °C, which is the temperature of the onset of crystallisation in the absence of the promoting agent. Under these conditions, there is also an increase in the number of strong acid centres ($H_0 \leqslant -5.6$).

The specific surface and hence the catalytic activity increase simultaneously. This effect has been explained by the formation of an amorphous layer of niobium phosphate on the surface of niobic acid.

Niobic acid is formed as an intermediate in the synthesis of niobium and its compounds. Very pure niobic acid is obtained on hydrolysis of the readily available and cheap chloride $NbCl_5$.[2] Different methods of preparation of niobic acid and of catalysts based on it have been described in greater detail in a review.[2]

III. The use of niobic acid as a catalyst

Niobic acid subjected to a preliminary vacuum heat treatment up to 200–220 °C exhibits a high activity in the hydration of ethylene to ethanol.[1,14] In the stationary state at 200–220 °C, it is 2–3 times more active than solid phosphoric acid, widely used as a catalyst in industry. The selectivity in the conversion of ethylene into ethanol exceeds 97%, acetaldehyde being formed as a side product. Niobic acid ($Nb_2O_5 \cdot nH_2O$, purity 99.8%), produced by the CBMM Company, was used in the reaction after being washed with distilled water, dried at 100 °C, and then evacuated at different temperatures for 2 h. The reaction was carried out in a reactor with a stationary catalyst bed and ethylene and water vapour pressures of 48 and 7.3 kPa. The unreacted ethylene was recycled. The activity of niobic acid gradually increased during the process and attained a constant value after 6 h. Deactivation of the catalyst was not observed. Best results were obtained at 200–220 °C. At 180 °C, the activity of niobic acid was lower. Ogasawara et al.[14] concluded that niobic acid is suitable for the industrial hydration of ethylene to ethanol. Niobic acid is active even in the hydration of isobutene and propene.[2]

A solid acid catalyst for the hydration of ethylene to ethanol and the conversion of methanol into dimethyl ether was obtained by treating niobic acid with phosphoric acid.[15,16] Niobic acid was kept without stirring in 0.5 M H_3PO_4 and was then dried in air. Such treatment increased its thermal stability: crystallisation occurred at ~600 °C (instead of 435 °C) and the specific surface and the concentration of strong acid centres with $H_0 \leqslant -5.6$ increased. Phosphoric acid was found to be dispersed on the surface of niobic acid.

Niobic acid exhibited a high activity also in the hydration of dicyclopentadiene.[17] At 170 °C and atmospheric pressure, the degree of conversion of dicyclopentadiene was 17%, which is 3–10 times higher than in the case where ion-exchange resins, SiO_2, TiO_2, Al_2O_3, TiO_2-SiO_2, and $SiO_2-Al_2O_3$ are used (Table 2). At 400 °C the activity of niobic acid fell sharply with a simultaneous decrease also in the acidity of its surface ($H_0 \leqslant 0.5$).[17]

Table 2. The activities of niobic acid and other catalysts in the hydration of dicyclopentadiene.[17]

Catalyst	Temperature of preliminary treatment/°C	Reaction temperature/°C	Conversion into alcohol (%)
Amberlist	–	100	2.0
Nafion H	–	150	0.3
Nafion H	–	170	0.4
SiO_2	400	170	2.0
TiO_2	400	170	5.2
Al_2O_3	400	170	3.1
$SiO_2-Al_2O_3$	500	170	4.0
TiO_2-SiO_2 {[Ti]/[Si] = 9}	500	170	4.3
Niobic acid	300	170	17.0

Niobic acid heat-treated at 100–600 °C is a highly active and selective catalyst of the isomerisation and hydration of phenyloxiran under mild conditions.[18] The isomerisation occurs on Lewis acid centres, while hydration occurs on Brønsted centres. In terms of its hydrophilic properties, niobic acid is more suitable for hydration than the $SiO_2-Al_2O_3$ system, H-ZSM, and H-silicalite, because it exhibits affinity both for water and the organic substrate. The hydrophilicity of the surface of niobic acid and the concentrations of the Brønsted and Lewis acid centres are regulated by the heat treatment temperature.[18] The monoamide $NC(CH_2)_nCONH_2$ has been obtained by hydrating the dinitrile $NC(CH_2)_nCN$ (n = 2–6) with niobic acid as the catalyst.[19]

Niobic acid is also an active and selective dehydration catalyst. $Nb_2O_5 \cdot nH_2O$ specimens evacuated at 100–200 °C showed a high activity, close to that of the $SiO-Al_2O_3$ system, in the dehydration of 2-butanol. The yield of but-2-ene was then higher than that of but-1-ene. Heat treatment of niobic acid at 300 °C induced a sharp decrease in its activity in the dehydration reaction, since this entailed a decrease in the number of Brønsted acid centres catalysing the dehydration reaction.[1] The high selectivity in the formation of olefins is due to the fact that Nb_2O_5 is a very stable oxide, which is hardly reduced under the reaction conditions. Niobic acid exhibited also a high activity and selectivity in the dehydration reactions of butane-1,4-diol and cyclopentanol.[2]

Niobic acid treated with 0.05–5 M H_3PO_4 solution exhibits a catalytic activity in the dehydration of cyclohexanol and in the alkylation of benzene by methanol.[13,20] The dehydration was carried out in a flow reactor at 180 °C, while benzene was alkylated in a pulse reactor at 400 °C using the ratio $[CH_3OH]/[C_6H_6]$ = 3. Best results were obtained when niobic acid was treated with 1 M H_3PO_4 solution (quantitative data are not quoted).[20] The addition of H_3PO_4 prevents the crystallisation of niobic acid and increases the acidity of its surface by virtue of the formation of an amorphous layer of niobium phosphate on the latter.[13]

Niobic acid is an effective catalyst of the esterification of acetic acid by ethanol at 120–160 °C (Table 3). When the reaction was carried out in the gas phase at 120 °C in the course of 1 h using the ratio $[C_2H_5OH]/[CH_3COOH]$ = 1, a rate of supply of 2.3 ml h^{-1}, and a niobic acid heat treatment temperature of 200 °C, the degree of conversion was 72% and the selectivity was 100%. The catalyst retained its activity throughout the period of 60 h during which the tests were carried out. In terms of its activity, it is superior to ion-exchange resins, $SiO_2-Al_2O_3$, and the solid superacids $ZrO_2-SO_4^{2-}$, $TiO_2-SO_4^{2-}$, and $Fe_2O_3-SO_4^{2-}$. A high and stable activity is also manifested by the zeolite H-ZSM-5 (the degree of conversion was 82%–99%, but the selectivity was lower, amounting to 72%–92%), diethyl ether and ethylene being formed as side products.

An increase in the heat treatment temperature of $Nb_2O_5 \cdot nH_2O$ from 120 to 300 °C leads to an increase in the number of acid centres with $H_0 = -8.2$. The active centres of the catalyst heat-treated at 120 °C are the numerous centres with H_0 up to -5.6. The likely usefulness of niobic acid as the catalyst of esterification reactions is due to its stability, activity, selectivity, and the ability to replace sulfuric acid, which is corrosive, leads to the appearance of a large amount of waste, and is difficult to regenerate. Cation-exchange resins are also inferior to niobic acid: they have a lower acidity and thermal stability, tend to swell, are fairly expensive, difficult to utilise in the spent state, etc.[1]

Esterification of methacrylic and acrylic acids by methanol occurred especially effectively on niobic acid with strong acid centres formed as a result of its heat treatment at 200 °C.[1]

Niobic acid subjected to preliminary heat treatment at 200–400 °C exhibits a high activity in the hydrolysis of acrylate in the presence of a large amount of water in the reaction medium.[1,21] The selectivity is 100%.

Table 3. The activities and selectivities of $Nb_2O_5 \cdot nH_2O$ and other solid acids in the esterification of ethanol by acetic acid.[1]

Catalyst	Heat treatment temperature/°C	Reaction temperature/°C	Conversion of ethanol (%)	Selectivity (%)	Side products
$Nb_2O_5 \cdot nH_2O$	200	120	72	100	–
		140	86	100	–
Sulfonic acid cation exchange resin	120	120	38	<99	–
		140	50	<98	–
$ZrO_2-SO_4^{2-}$	500	140	56	90	$(C_2H_5)_2O$
$Fe_2O_3-SO_4^{2-}$	500	140	13	93	$(C_2H_5)_2O$
$TiO_2-SO_4^{2-}$	500	120	95 (94)[a]	99 (98)[a]	
		140	100	95	C_2H_4
$SiO_2-Al_2O_3$	–	120	4	99	$(C_2H_5)_2O + C_2H_4$
		140	14	98	
H-ZSM-5	–	120	82	92	$(C_2H_5)_2O + C_2H_4$
		140	99	72	

Note. The mass of the catalyst was 1 g and the reaction time was 1 h.
[a] The reaction time was 2 h.

Niobic acid is an active and selective catalyst of condensation reactions.[2,3]

Isoprene can be obtained in 61% yield in one stage from isobutene and formaldehyde on $Nb_2O_5 \cdot nH_2O$ at 350 °C. After 50 h the yield falls to 54%.[22]

Condensation of butyraldehyde at 160 °C on $Nb_2O_5 \cdot nH_2O$ affords 2-ethylhexanol. The degree of conversion is 92% and the selectivity is 96%.[23]

2,5-Dimethylhexa-2,4-diene has been obtained[24] on condensing isobutene and isobutyraldehyde at 200 °C in the presence of niobic and sulfuric acids:

Catalyst	Conversion (%)	Selectivity (%)
$Nb_2O_5 \cdot nH_2O$	97	82
H_2SO_4 (16 mass%)	99	21

Evidently, niobic acid ensures a higher selectivity than sulfuric acid.

According to Japanese workers,[25] isobutyl methyl ketone can be obtained from acetone and H_2 in the presence of 0.1% $Pd/Nb_2O_5 \cdot nH_2O$. At 160 °C and a pressure of 2 mPa, the degree of conversion of acetone was 41.8% and the selectivity was 93.5%. Under the same conditions, the degree of conversion in the presence of the 0.1% Pd/Al_2O_3 catalyst did not exceed 3.8% and the selectivity did not exceed 62.3%.

Niobic acid catalyses also olefin isomerisation and polymerisation processes. $Nb_2O_5 \cdot nH_2O$ evacuated at 100 °C proved to be the most active catalyst in the isomerisation of but-1-ene.[1] After evacuation at 300 °C, the activity of the catalyst fell sharply, but it was almost completely restored after the introduction of water vapour and subsequent evacuation at 100 °C (Fig. 4). Hence it was concluded that the isomerisation reaction is activated mainly by the Brønsted acid centres, the number of which diminishes with increase in the evacuation temperature. After evacuation at 500 °C, treatment with water vapour does not restore the activity of the specimen. The phase transition, occurring at 500 °C and accompanied by a decrease in surface area, precludes the regeneration of the Brønsted acid centres.[1]

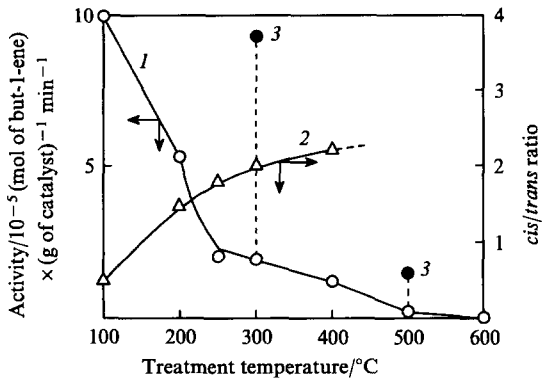


Figure 4. The activity (curve *1*), and selectivity (curve *2*) of niobic acid in the isomerisation of but-1-ene; the activity of the catalyst after its treatment with water and subsequent evacuation at 100 °C (curve *3*).

In the polymerisation of propene, niobic acid exhibits a high activity after being evacuated at 100 °C. Evacuation at 150–200 °C lowers the activity and after heat treatment at 250–300 °C the activity again increases (Fig. 5). After heat treatment at 500 °C, the activity vanishes.[1,12] Such a change in activity is explained by the fact that in the low-temperature heat treatment the polymerisation is catalysed by the Brønsted centres, but when the temperature of the heat treatment is 250–300 °C the catalysis is effected by the Lewis centres.[1]

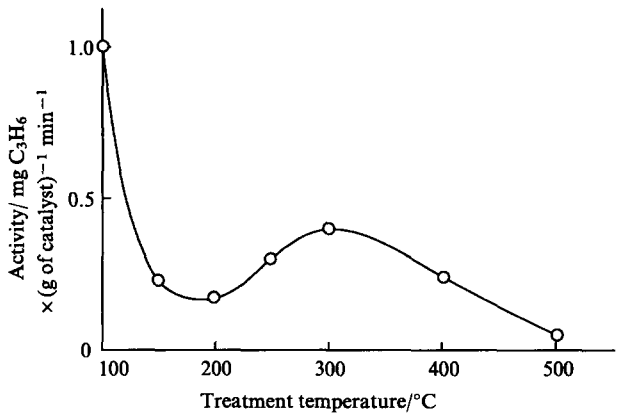


Figure 5. Dependence of the activity of $Nb_2O_5 \cdot nH_2O$ in the polymerisation of propene on the temperature of the heat treatment of the catalyst.

Much attention has been devoted to deposited catalysts based on niobic acid.[26–33] The stability of these catalysts is satisfactory and they crystallise and are reduced at higher temperatures than niobic acid. Catalysts obtained by depositing niobic acid on SiO_2 are especially effective. It has been suggested that the change in the properties of the deposited Nb_2O_5 is caused by the strong interaction at the $SiO_2-Nb_2O_5$ interface with formation of the Nb–O–Si linkage.

Amorphous Nb_2O_5, formed as a monolayer on SiO_2, has been tested[26] as a catalyst of the dehydration of ethanol to ethylene. The catalyst was prepared by depositing $Nb(OC_2H_5)_5$ on SiO_2 and subsequent treatment with H_2O and O_2. Its activity was manifested at 100–300 °C and exceeded by 1–2 orders of magnitude the activity of niobic acid without a carrier. The selectivity was 100%. The catalytic properties of mononuclear, dinuclear (0.1%–1% Nb_2O_5), and monolayer (2%–8% Nb_2O_5) niobium oxide catalysts, deposited on SiO_2 via the interaction of the OH groups with $Nb(\eta^3\text{-}C_3H_5)$, $[Nb(\eta^5\text{-}C_5H_5)H\text{-}\mu\text{-}(\eta^5,\eta'\text{-}C_5H_4)]_2$ and $Nb(OC_2H_5)_5$ respectively, have also been investigated.[27]

Analysis by the method of extended X-ray absorption fine structure (EXAFS) established that the niobium centres are fixed on the surface via the oxygen atoms (Nb–O–Si). The mononuclear niobium oxide centres are active in the dehydrogenation of ethanol at 250 °C, the selectivity in the formation of CH_3CHO reaching 96.1%. Dehydration with formation of 45% of ethylene and 52.7% of diethyl ether takes place on the dinuclear niobium centres at 250 °C.[27,28] The monolayer niobium catalyst 8% Nb_2O_5/SiO_2 is 20 times more active at 300 °C than niobic acid in the esterification of acetic acid by ethanol.[29] It has been suggested that its activity is determined by the Lewis acid centres. The catalyst is stable up to 600 °C. For a niobium content in the catalyst up to 8%, a thin homogeneous amorphous layer of niobic acid is formed on the SiO_2 surface.[29] The structure, acidity, and reactivity of Nb_2O_5 deposited on the MgO, Al_2O_3, TiO_2, ZrO_2, and SiO_2 surfaces have been investigated in the model methanol oxidation reaction.[30,31] Lewis acid centres are present on the surfaces of all the systems but, when niobic acid is deposited on the SiO_2 and Al_2O_3 surfaces, their activity is highest. On the SiO_2 surface, the Lewis acid centres exhibit oxidation-reduction properties, formaldehyde, and methyl formate being formed preferentially from methanol. On the other hand, on the Al_2O_3 surface they behave as acid centres, dimethyl ether being formed from methanol.[30] Brønsted acid centres are also present on the surfaces of the Nb_2O_5/SiO_2 and Nb_2O_5/Al_2O_3 catalysts.

The acidity of niobic acid and its capacity for crystallisation and reduction depend on the starting materials employed, the presence of impurities, and the method of deposition of niobic

acid on carriers.[32] Whereas pure amorphous Nb_2O_5 crystallises as the T-Nb_2O_5 phase after treatment at 500 and 600 °C and as the H-Nb_2O_5 phase at 1000 °C and begins to be reduced at temperatures above 600 °C, Nb_2O_5 present in catalysts obtained by impregnating SiO_2 with a solution of ethoxyniobium in hexane and sputtered onto the SiO_2 surface from the gas phase crystallises and is reduced at higher temperatures.[33] The catalyst obtained by impregnation is particularly effective. It has been suggested[33] that the change in the properties of the deposited Nb_2O_5 is caused by the strong interaction at the $SiO_2-Nb_2O_5$ interface, which influences not only the first monolayer but also the subsequent Nb_2O_5 layers as a consequence of the formation of Nb–O–Si linkages.

IV. The use of niobium oxide as a carrier and promoting agent

Hydrated niobium oxide is not the only niobium compound of interest for catalysis. Niobium oxides can also be used as promoting agents and carriers. For example, Nb_2O_5 used as a carrier in rhodium catalysts for the synthesis of higher hydrocarbons from CO and H_2 exerts a strong influence on the activity and selectivity.[3] The effectiveness of the carriers diminishes in the sequence $Nb_2O_5 > ZrO_2 > Al_2O_3 > SiO_2 > MgO$. At 220 °C the degree of conversion of CO on Rh/Nb_2O_5 reaches 76%,[3] whereas on Rh/Al_2O_3 it is only 1.4%.

The $Rh-Nb_2O_5$ interaction in the niobium pentoxide-promoted Rh/SiO_2 catalyst has been investigated by X-ray powder diffraction, X-ray photoelectron spectroscopy, IR spectroscopy, the EXAFS method, and the method based on the chemisorption of H_2 in relation to the test reaction involving the hydrogenolysis of ethane.[34,35] The degree of interaction of Rh with Nb_2O_5 depended on the heat treatment temperature. After heat treatment in air at 700 and 900 °C, strong interaction of rhodium with Nb_2O_5, involving the formation of the $RhNbO_4$ phase, was observed. Heat treatment at 500 °C did not give rise to this effect.

The strong metal–carrier interaction influences the hydroformylation of ethylene in the presence of palladium catalysts deposited on Nb_2O_5.[36] The influence of the temperature in the reduction with hydrogen on the chemisorption and catalytic properties of the 5% Pd/Nb_2O_5 and 5% Pd/SiO_2 catalysts has been investigated by X-ray powder diffraction and IR spectroscopy. The amounts of H_2 and CO chemisorbed on Pd/Nb_2O_5 reduced at 500 °C were respectively almost 4 and 2.5 times smaller than on Pd/Nb_2O_5 reduced at 200 °C. A strong metal–carrier interaction was observed in the catalyst reduced at 500 °C and the main product of the reaction of ethylene, CO, and H_2 at 64 °C was 2-methylpenten-2-al. Ethylene was hydrogenated to ethane on Pd/Nb_2O_5 reduced at 200 °C and on Pd/SiO_2.[36]

A strong promoting influence of Nb_2O_5 has been observed in a number of reactions.[3,37–39] For example, the $Pt/Nb_2O_5/SiO_2$ catalyst, in which the degree of coverage of Nb_2O_5 did not exceed the monolayer coverage, proved to be 40 times more active than Pt/SiO_2 and 1000 times more active than Pt/Nb_2O_5 in the hydrogenation of ethylene.[37]

The addition of Nb_2O_5 to V_2O_5/TiO_2 and to Fe_2O_3 appreciably improved the activity of the latter in the decomposition of NO using NH_3 as the reducing agent.[3]

$$4NO + 4NH_3 + 3O_2 \longrightarrow 4N_2 + 6H_2O\,.$$

On the catalyst having the composition (5% V_2O_5 + 2.7% Nb_2O_5)/TiO_2, the degree of conversion of NO at 200 °C was 100% whereas on the catalyst 7.5% V_2O_5/TiO_2 it was 40% at the same temperature and reached 100% only at 300 °C. The degrees of conversion of NO (expressed as percentages) on these catalysts varied as a function of the duration of the process in the following way:[3]

	Initial	After 15 h	After 30 h
$(V_2O_5-Nb_2O_5)/TiO_2$	99	94	89
V_2O_5/TiO_2	40	12	7

The use of the Rh/SiO_2 catalyst modified with Nb_2O_5 for the reduction of NO by ammonia has been examined.[38]

An active catalyst for the Fischer–Tropsch synthesis includes Ru/TiO_2 modified with 0.5%–25% of the oxide of a metal belonging to the Nb, V, and Ta group or their mixture in a non-crystalline form.[39]

V. Other niobium compounds used in catalysis

Other niobium compounds have also found applications in catalysis. Niobium sulfides, prepared by direct synthesis from the elements, are extremely active in the reactions involving the hydrogenation of biphenyl, toluene, and cyclohexene.[40] Their activity diminishes in the sequence $NbS_3 > NbS_2 > Nb_{1.12}S$. They exhibit the highest activity and selectivity (>80%) in the cracking reaction.[40] Niobium sulfides are much more active than vanadium and ruthenium sulfides in the cracking and hydrodenitrogenation reactions.[41,42]

A series of niobium compounds exhibit a photocatalytic activity on irradiation with visible light.[43–45] Thus $K_4Nb_6O_{17}$ is extremely active in the photolysis of water.[44,45]

$$H_2O \longrightarrow H_2 + \tfrac{1}{2}O_2\,.$$

When 1% Ni is deposited on $K_4Nb_6O_{17}$, the activity of the latter increases.[45] A niobium-based catalyst for the metathesis of propene has been described.[46] A heterogeneous catalyst based on molybdenum or niobium chlorides deposited on SiO_2 is active in the reactions of unsaturated compounds—metathesis, cyclotrimerisation, and alkylation.[47] The catalytic and sorption properties of an aerosilogel modified with $NbCl_5$ in the ethanol decomposition reaction at 300 °C have been examined.[48]

The isomerisation and oligomerisation of olefins on the Nb_2O_5 and Nb_2O_5/SiO_2 catalysts reduced in a mixture of H_2 and H_2O at 600 °C have been investigated. The catalysts exhibited an activity in the isomerisation of *cis*-but-2-ene at 25 and 100 °C. It has been established by the EPR method[50] that the active catalytic centres are isolated coordinatively-unsaturated Nb^{4+} cations, which are more stable on the SiO_2 surface.

The high concentration of strong acid centres on the surface of crystalline β-Nb_2O_5, obtained by dissolving Nb_2O_5 in concentrated H_2SO_4 and subsequent crystallisation at 120 °C, is responsible for its activity in dehydration and esterification reactions.[51]

Amorphous and crystalline niobium phosphates,[52–54] which can be readily synthesised from niobium sulfate and phosphoric acid, may be of practical interest as acid catalysts.[52,53] The influence of the temperature of the preliminary treatment on the texture and acid and catalytic properties of niobium phosphate has been investigated by differential thermal analysis, thermogravimetric analysis, X-ray powder diffraction, the adsorption and indicator methods, the IR spectroscopy of adsorbed pyridine, and the test reactions involving the dehydration of 2-butanol, the isomerisation of but-1-ene, and the polymerisation of propene.[54] An increase in the heat treatment temperature diminishes the specific surface and the pore volume in the catalyst (Table 4). After heat treatment in the temperature range 100–500 °C, both Lewis and Brønsted acid centres with $H_0 = -8.2$ are present on the surface of the phosphate (Fig. 6). The catalyst treated at 150 °C is most active in the dehydration of 2-butanol, while the catalysts treated at 250 and 300 °C respectively are most active in the but-1-ene isomerisation and propene polymerisation reactions. Niobium phosphate is a more stable and active catalyst than niobic acid.

Table 4. The specific surfaces, pore volumes, and average pore diameters of niobium phosphate treated at different temperatures (niobium concentration in the specimen 43.44%).[54]

Treatment temperature/°C	Specific surface/$m^2\ g^{-1}$	Pore volume/$cm^3\ g^{-1}$	Average pore diameter/Å
150	277	0.352	34.8
300	230	0.310	39.0
500	182	0.287	39.0

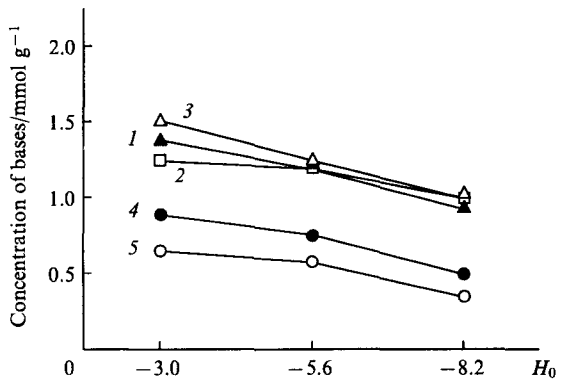


Figure 6. Distribution of the centres with respect to their acid strength in niobium phosphate heat-treated at different temperatures (°C): *1*, 100; *2*, 150; *3*, 300; *4*, 400; *5*, 500.

By adding phosphoric acid to a solution obtained when Nb_2O_5 is dissolved in concentrated H_2SO_4 in the presence of $(NH_4)_2SO_4$ and by subsequent addition of NH_4OH until the attainment of pH 1, the crystalline niobium(V) phosphate was isolated. It crystallises in a pseudocubic lattice with a_0 = 10.244 Å and has the rigid three-dimensional structure of a zeolite.[53] Its empirical formula was determined as $Nb_2O_5 \cdot 1.5P_2O_5 \cdot 7.5H_2O$, while its chemical formula was found to be $(NbO)_2 \cdot (HPO_4)_3 \cdot 6H_2O$. The crystalline niobium phosphate was characterised by pH titration, IR and X-ray photoelectron spectroscopy, X-ray powder diffraction, thermogravimetric analysis, and differential scanning calorimetry. It was established that its chemical stability is higher than that of the amorphous phosphate and that it has a high exchange capacity, reaching 4.6 mmol g^{-1} for K^+ (the theoretical value is 4.8 mmol g^{-1}). According to Okazaki,[2] both the amorphous and crystalline niobium(V) phosphates can be used either as catalysts or as carriers in many processes.

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