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Catalytic application of niobium compounds

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Abstract

Salient examples of catalytic application of niobium compounds and materials are demonstrated. Niobium oxides, when small amounts are added to known catalysts, markedly enhance catalytic activity and selectivity and prolong catalyst life for various reactions. Moreover, niobium oxides exhibit a pronounced effect as supports of metal or metal oxide catalysts. Hydrated niobium pentoxide (niobic acid, $Nb_2O_5 \cdot nH_2O$) and niobium phosphate which are unusual solid acids show high catalytic activity, selectivity, and stability for acid-catalyzed reactions. Layer compounds containing niobium combined with metal show peculiar photocatalytic activity. These characteristic features of niobium compounds as catalysts and catalyst components are discussed, their potential significance being emphasized.

Keywords: Niobium compounds; Catalytic application

1. Introduction

Niobium compounds and materials are now interesting and important catalysts for various reactions. Although there are few differences in electronegativity and ionic radius between Nb and its neighbors (V, Zr, Mo) in the periodic table of elements (Fig. 1), it is intriguing that the catalytic behaviors of niobium compounds are quite different from those of the surrounding elements' compounds. Thus, the research and development on the catalytic application of niobium compounds have been very active for the last 20 years.

The characteristic features of niobium compounds are the promoter effect and the support effect. Niobium oxides remarkably enhance catalytic activity and prolong catalyst life when the small amounts are added to known catalysts. Moreover, niobium oxides exhibit a pronounced effect as supports of metal and metal oxide catalysts. Mixed oxides containing niobium and niobium oxide supported on the other oxides also show the above effect.

Generally speaking, niobium oxide and the mixed oxides including Nb_2O_5–SiO_2, Nb_2O_5–Al_2O_3, Nb-zeolite, mesoporous Nb-MCM-41, Nb-layer compounds, etc. have redox property, acidic property and/or photosensitivity, which cause interesting catalytic behaviors.

Hydrated niobium pentoxide, $Nb_2O_5 \cdot nH_2O$, which is usually called niobic acid, and niobium phosphate (NbPO) have strong acidic properties on the surfaces and are used as solid acid catalysts. In particular, niobic acid containing large amounts of water exhibits high catalytic performances for acid-catalyzed reactions in which water molecules participate or are liberated.

In this paper, the most salient examples of catalytic application of niobium compounds are reviewed and discussed for their significance. For details of various reactions catalyzed by niobium compounds, refer to a review article published in 1995 [1] and for those of preparation, characterization, and catalytic application of niobium compounds, a recent review published in 1999 is useful [2]. Some other reviews on "Niobium,

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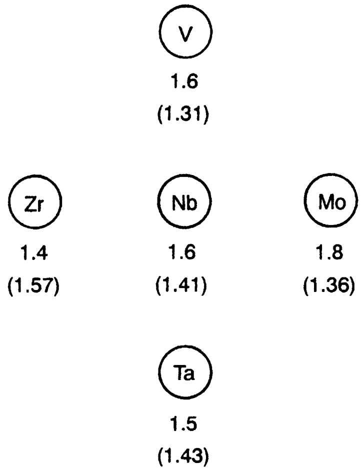


Fig. 1. Location of niobium in periodic table. The values without and with parentheses denote electronegativity and ionic radius, respectively.

catalyst repair kit" [3], "Application of niobium oxides as catalysts" [4], and "Niobic acid as an unusual acidic materials" [5] are also given in references in this paper.

There are some reports on catalytic application of organometallic compounds of niobium in homogeneous phase. However, this paper is limited to heterogeneous catalysis by solid niobium compounds, since the heterogeneous catalysis is becoming even more important for establishing less cost and environmentally clean processes.

2. Promoter effect

2.1. Oxidative dehydrogenation of alkanes

The potential use of cheap alkanes such as ethane and propane as sources of the corresponding olefins such as ethylene and propylene from which various important chemicals, drugs, polymers are obtained is becoming important.

Union Carbide disclosed an invention that ethane is oxidatively dehydrogenated to ethylene at high conversion and selectivity using mixed metal oxide catalysts containing Mo, V, and Nb [6]. As shown in Table 1, the catalytic activity (the temperature at which 10% conversion of ethane could be achieved) of $Mo_{16}V_4Nb_2$ oxide is remarkably high compared to those of the other mixed oxides, the selectivity for ethylene formation being 100%, indicating the importance of the promoter effect of Nb. In a conventional flow reactor experiment where the feed gas composition (vol.%) is ethane 9%, oxygen 6%, nitrogen 85%, space velocity is 340 h^{-1}, and the pressure 1 atm, the catalyst shows again the highest activity (29% conversion) with considerably high selectivity (83%) at 300 °C. Under the high pressure conditions (75–125 psig) using an autoclave, the $Mo_{16}V_{4.6}Nb_{0.6}$ catalyst exhibits 69–75% conversion with 68–71% selectivity.

Table 1
Catalytic activities and selectivities for oxidative dehydrogenation of ethane to ethylene by a pulse method [6][a]

Metal oxide catalyst (composition)	Temperature for 10% conversion of C_2H_6 (°C)	Selectivity to C_2H_4 (%)
Mo	500	88
$Mo_{16}Mn_{16}$	550	35
$Mo_{16}Nb_4$	634	74
$Mo_{16}Ti_4$	600	65
$Mo_{16}V_4$	540	100
$Mo_{16}V_4Fe_1$	435	87
$Mo_{16}V_4Mn_4$	505	100
$Mo_{16}V_4Nb_2$	286	100

[a] Two milliliters pulses of feed gas consists of ethane 8.0 vol.%, oxygen 6.5 vol.%, and balance nitrogen was diluted by helium carrier gas (60 ml/min) and carried over 3.0 g catalyst.

The promoter effect of Nb_2O_5 as an additive to a MoO_3–V_2O_5 catalyst for the same reaction was reported also by Burch and Swarnaka [7]. MoO_3–V_2O_5–Nb_2O_5 (atomic ratio = 6:3:1) shows a higher catalytic activity than MoO_3–V_2O_5 (atomic ratio = 6:3) at 390 °C, the selectivity (81%) of the former catalyst being also higher than the selectivity (61%) of the latter catalyst.

According to Somorjai and coworkers [8], the presence of all three oxides (MoO_3, V_2O_5, and Nb_2O_5) together is necessary in order to have active and selective catalysts and the highest selectivity (93%) is obtained when the ratio of Mo:V:Nb is 19:5:1. The active phase is based on MoO_3 and V_2O_5. The role of Nb_2O_5 is to enhance the intrinsic activity of Mo–V combination and improve the selectivity by inhibiting the total oxidation of ethane to carbon dioxide. Recently, Ruth et al. [9,10] studied the preparation, morphology, and reducibility of Mo–V–Nb catalysts and discuss their roles for the formation of ethylene and acetic acid from ethane.

In the oxidative dehydrogenation of propane to propylene, Smits et al. [11] found that Nb_2O_5 itself calcined at 650 °C shows a high selectivity of 85% at 540 °C, though the conversion is low. The conversion increases with increasing the partial pressure of oxygen and reaction temperature. With 10% O_2, the conversion reaches to about 10% at 605 °C, the selectivity being 60% over Nb_2O_5. The addition of V_2O_5 (1 mol%) to Nb_2O_5 causes 100% oxygen conversion with 70% selectivity at 400–500 °C [12]. The reaction of butane is easier than those of ethane and propane. A Nb_2O_5–Cr_2O_3/ZrO_2 catalyst is reported to form butenes from butane at 450 °C [13].

2.2. Oxidative coupling of methane

For the oxidative coupling of methane which is an important reaction to utilize natural gas, the catalytic activity of Li/Nb/MgO was found to be 10 times higher than that of Li/MgO by Ross and coworkers [14]. They examined the promoter effect of various additives in the case of Li–Na/MgO catalyst. As shown in Fig. 2, the C_2 (ethane and ethylene) yield is the highest when Nb is added in the range of reaction temperature of 650–775 °C [15,16]. The promoter effect is in the order of Nb > Sn > Zr, while negative effect is seen for Co addition.

2.3. Oxidation and ammoxidation

The addition of niobia to bismuth molybdate catalyst is well known to enhance the catalytic activity and selectivity for the oxidation and ammoxidation of olefins [3,17]. Recently, a pronounced promoter effect of niobia on the catalytic performance of Mo–V–Te mixed oxide for the oxidation and ammoxidation of propane to acrylic acid and acrylonitrile, respectively, have been reported by Mitsubishi Chemical [18]. Acrylic acid is a useful chemical as a raw material for various synthetic resins, high water-absorbent materials, paints, etc. which is produced from propylene in the scale of several million tons per year in the world. Thus, the production of acrylic acid from cheap propane has been an important R&D subject. The catalyst disclosed by Mitsubishi Chemical is $Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_n$ which exhibits 84.2% propane conversion and 62.5% acrylic acid selectivity, the yield being 52.5% at reaction temperature of 380 °C [18]. Reaction gas mixture of propane:air:steam = 1:15:14 (volume ratio) is supplied into the catalyst bed with the rate of 0.10 g propane/g cat h. It is a really surprising result, because the yield obtained hitherto was less than 20%.

In the case of the ammoxidation of propane to acrylonitrile, the same component catalyst as above

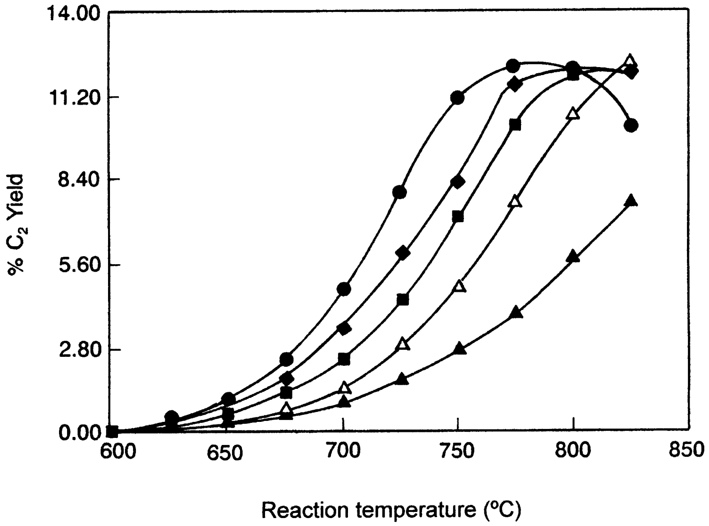


Fig. 2. Variation in percentage C_2 yield with reaction temperature in oxidative coupling of methane over Li–Na–X/MgO catalysts. Gas feed composition, CH_4 (76 kPa), O_2 (7 kPa), He (18 kPa); flow rate, 100 ml/min. (▲) X=Co; (△) no X; (■) X=Zr; (◆) X=Sn; (●) X=Nb [15].

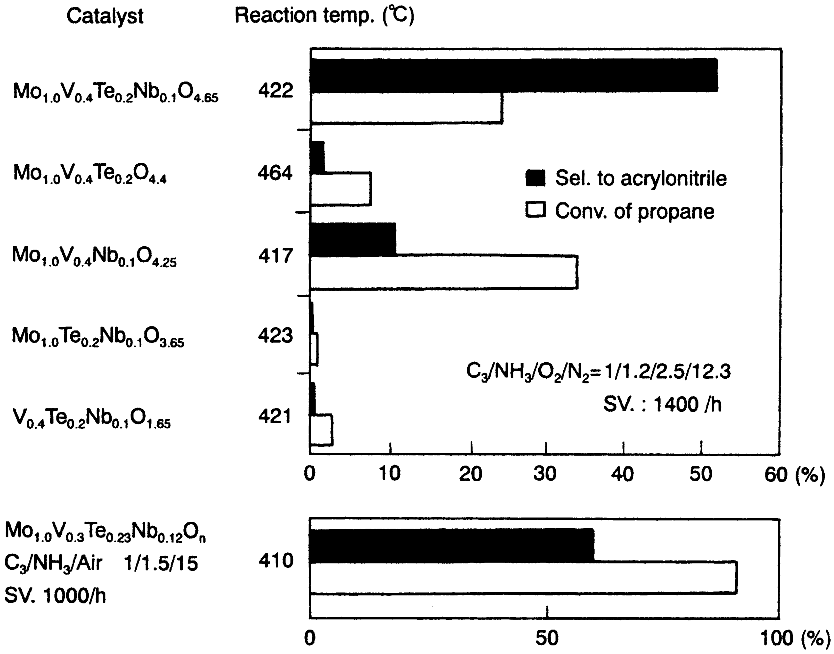


Fig. 3. Promoter effect of Nb on activity and selectivity of Mo–V–Te–Nb–O catalyst for ammoxidation of propane [20].

shows 91.5% propane conversion and 63.7% selectivity, the yield of acrylonitrile being 58.3% [19]. In order to clarify the contribution of each component to the catalytic activity and selectivity, the catalytic performances of Mo–V–Te, Mo–V–Nb, Mo–Te–Nb, and V–Te–Nb were examined. As shown in Fig. 3, the catalytic activity and selectivity of Mo–V–Te without Nb are only several percentage, indicating that Nb is an essentially necessary component of the catalyst [20]. We see Mo–V is vitally important components and the promoter effects of Nb and Te are also important for enhancing both activity and selectivity.

The reaction pathways of the selective oxidation of propane over the MoVTeNbO catalyst and some structural aspects of the catalyst are discussed recently in a review paper by Lin [21].

The mild oxidation of *n*-butane (*n*-C_4) to maleic anhydride (MA) by using vanadium phosphorus oxide (VPO) as a catalyst has been already industrialized. It is still desired to enhance the activity and selectivity of the catalyst and diminish the time required for activating the catalyst with *n*C_4/air flow. Recently, Pries de Oliveira et al. [22] reported that the addition of NbPO to VPO catalyst improves the catalytic performance, as shown in Table 2. The VPO–NbPO catalysts reach a stationary state after only 40 h, while the VPO catalyst alone needs more than 120 h. The addition of NbPO also improves the mechanical strength of VPO pellets to be used in fixed bed reactors.

2.4. Removal of nitrogen oxides

Decomposition of NO in industrial stack gas is important in preventing air pollution. Removal of NO by

Table 2
Promoter effect of NbPO on catalytic activity and selectivity of VPO for mild oxidation of *n*-butane (*n*-C_4) to MA [22][a]

Catalysts	*n*-C_4 conversion (%)	MA selectivity (%)	MA yield (%)
VPO	40	62	24.8
VPO–NbPO (lgNbPO/3.2 g V_2O_5)	60	75	45
VPO–NbPO (0.5 g NbPO/3.2 g V_2O_5)	75	75	54.2

[a] Measured after 40 h of activation at 400 °C of the precursors. *n*-C_4/O_2/He = 1.6/18/80.4; VSHV = 1500 h^{-1}.

Table 3
Effect of Nb_2O_5 addition on activity of V_2O_5/TiO_2 catalyst for reaction of NO with NH_3 at 200 °C (NO: 300 ppm, NH_3: 450 ppm, SO_2: 500 ppm, O_2: 15% [3,23])

Catalysts	Initial conversion (%)	Conversion after 15 h (%)	Conversion after 30 h (%)
V_2O_5–Nb_2O_5/TiO_2[a]	99	94	89
V_2O_5/TiO_2[b]	40	12	7

[a] Contents of V_2O_5 and Nb_2O_5 are 5 and 2.7 wt.%, respectively.
[b] Contents of V_2O_5 is 7.5 wt.%.

decomposition uses NH_3 as a reducing agent:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \quad (1)$$

The most popular catalyst for this process is V_2O_5 supported on TiO_2, which shows a practical activity between 300 and 400 °C. However, in coking furnaces or calcination plants used in the steel industry, the emission gas temperatures are <300 °C, so the catalyst must be active at low temperatures. Addition of Nb_2O_5 to V_2O_5/TiO_2 improves the low temperature activity as shown in Table 3 [3,23]. Addition of Nb_2O_5 is also effective for stabilizing the catalyst and improving its mechanical strength.

For the same reaction, Fe_2O_3 becomes highly active if a small amount of Nb_2O_5 is added, as seen in Fig. 4 [1,24]. The catalyst, Nb_2O_5–Fe_2O_3 (Nb/Fe = 5/95), shows a high activity even in the presence of SO_2.

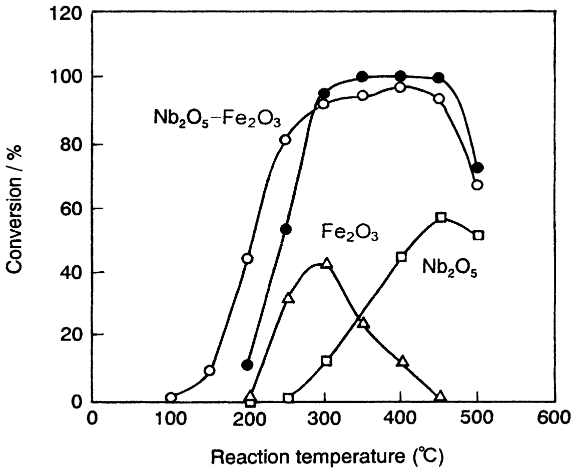


Fig. 4. Catalytic activity of Nb_2O_5–Fe_2O_3 (Nb/Fe = 5/95) for reaction of NO with NH_3. ○, without SO_2; ●, with SO_2 [24].

Table 4
Cumene transformation at 400 °C [2]

Catalyst	Cumene conversion (%)	Product distribution (%)		
		Propene	Benzene	*n*-Propyl benzene
NaY	3	2	4	90
NbNaY	61	51	47	2
NbNaY–H_2O	91	48	48	2

2.5. Cracking of cumene

Promoter effect of Nb on the catalytic performance of NaY zeolite is remarkable for cumene cracking. Nb–NaY obtained by cation exchange between NaY and an ethanol solution of $NbCl_5$ shows a high catalytic activity for cumene cracking to benzene and propylene at 400 °C, though NaY itself forms mainly *n*-propyl benzene, as shown in Table 4 [2].

3. Support effect

3.1. Hydrogenation

Both activity and selectivity of a metal catalyst supported on metal oxides for the formation of hydrocarbons from CO and H_2 are sensitive to the support oxide. A pronounced support effect of Nb_2O_5 on Rh catalyst for activity and selectivity towards high hydrocarbons was found in CO hydrogenation [25]. Fig. 5 shows that the support effect is in order of $Nb_2O_5 > ZrO_2 > Al_2O_3 > SiO_2 > MgO$. The conversion of CO over Rh/Nb_2O_5 is almost 76% at 220 °C in contrast to the negligible conversion (1.4%) over the conventional Rh/Al_2O_3 catalyst. In the case of Rh/Nb_2O_5, C_2–C_5 hydrocarbons are obtained in addition to methane. Over Co/Al_2O_3, a main product is methane, whereas C_5^+ over Co/Nb_2O_5 [26].

Kugler and Tauster reported that a Ni/Nb_2O_5 catalyst shows much higher conversion than a Ni/Al_2O_3 catalyst for CO hydrogenation [27]. Ko et al. [28] also reported that a Ni/Nb_2O_5 catalyst shows a higher selectivity toward olefinic hydrocarbons (C_2–C_4) compared to a Ni/SiO_2 catalyst and they explain the support effect in terms of a strong metal–support interaction (SMSI) between Nb_2O_5 and Ni metal.

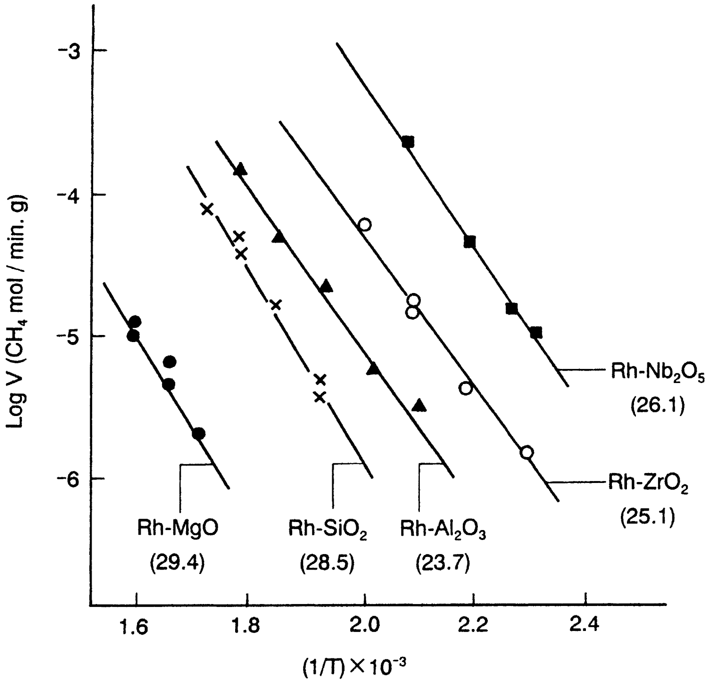


Fig. 5. Arrhenius plot of CO + H_2 reaction over Rh catalyst supported on various metal oxides. Values in parentheses show activation energies [25].

In the hydrogenation of 1,3-butadiene, the selectivities for butane, 1-butene, and 2-butenes are 78, 18, and 4%, respectively, over Pt/Al_2O_3 reduced at 500 °C, while 30, 45, and 25% over Pt/Nb_2O_5 reduced at the same temperature, indicating an increase in platinum electronic density on Pt/Nb_2O_5 caused by the SMSI effect. It is interesting that the selectivities are 60, 30, and 10% over Pt–Sn/Al_2O_3, whereas 10, 80, and 10% over Pt–Sn/Nb_2O_5 [29]. In this case, besides the SMSI effect, a bimetallic Pt–Sn interaction becomes important.

3.2. Methylisobutyl ketone synthesis

The support effect of niobic acid ($Nb_2O_5 \cdot nH_2O$) on a Pd catalyst is remarkable for the synthesis of methylisobutyl ketone (MIBK) from acetone [30]. The catalytic activity and MIBK selectivity of Pd/$Nb_2O_5 \cdot nH_2O$ are much higher than those of Pd/Al_2O_3 as shown in Table 5 and are maintained at the stationary levels for 1500 on-stream hours [30]. In this case, besides the SMSI effect, the strong acidic property of niobic acid plays an important role.

3.3. Metathesis

Methyltrioxorhenium (CH_3ReO_3) supported on $Nb_2O_5 \cdot nH_2O$ shows a pronounced catalytic activity for the metathesis of *cis*-2-pentene or 1-pentene, the reaction products being 3-hexene and ethylene or 4-octene and 2-butene. The reaction reaches the equilibrium in only 1 min when niobic acid is used as a support (Table 6) [31]. However, CH_3ReO_3 supported on SiO_2 or TiO_2 is inactive and the one supported

Table 5
Synthesis of MIBK from acetone [30][a]

Catalyst	Conversion (%)	Selectivity (%)		
		MIBK[b]	IPA[c]	DIBK[d]
Pd (0.1 wt.%)/ $Nb_2O_5 \cdot nH_2O$	41.8	93.5	0.3	3.6
Pd (0.1 wt.%)/ Al_2O_3	3.8	62.3	35.8	0.6

[a] Reaction temperature: 160 °C, pressure: 20 atm.
[b] Methylisobutyl ketone.
[c] Isopropyl alcohol.
[d] Diisobutyl ketone.

Table 6
Effects of various supports on catalytic activity of CH_3ReO_3 for metathesis of *cis*-2-pentene at room temperature [31]

Support[a]	Catalytic activity[b]
SiO_2 (500)[c]	None
TiO_2 (200)	None
MgO (400)	Very low
Nb_2O_5 (300)	Equilibrium in 1 min

[a] Re:support = 1:100 (w/w), except for TiO_2 (4:100).

[b] Solvent: chlorobenzene; room temperature. [Re]:[*cis*-2-pentene] = 1:100.

[c] ( ) refers to the evacuation temperature (°C) for a given support before CH_3ReO_3 chemisorption.

on MgO shows very low activity. The activity of $CH_3ReO_3/Nb_2O_5{\cdot}nH_2O$ becomes a maximum when the support is evacuated at 200–300 °C before the chemisorption of CH_3ReO_3. Since evacuation temperature dependence of the activity is similar to that of Lewis acidity of the support [32], Lewis acid sites are considered to play a role for the catalytic activity.

3.4. Hydrotreating reactions

The catalytic activity of Mo–Ni/Nb_2O_5–Al_2O_3 for sulfur and nitrogen removal from gas–oil is reported to be higher than that of Mo–Ni/Al_2O_3. The support effect of Nb_2O_5 is explained to be due to the increase of the surface acidity of the support [33]. The catalytic activities of presulfided Mo/Nb_2O_5 and Ni/Nb_2O_5 for the hydrocracking of cumene are higher than those of unsulfided catalysts. The activities remarkably change with the presulfiding conditions. On severe sulfiding with 15 mol% H_2S at 400 °C, the activity of Mo/Nb_2O_5 becomes 60 times higher than that of Mo/Al_2O_3 [34]. Niobium sulfide itself exhibits high catalytic activity for hydrotreating reactions of several model compounds [35]. The intrinsic activity of NbS_3 for the reactions is higher than that of MoS_2, showing remarkable selectivities in cracking and isomerization reactions.

3.5. Other reactions

For the dehydrogenation of cyclohexane, the turnover frequency of Pt/Nb_2O_5 catalyst is about eight times higher than that of Pt/Al_2O_3, indicating a big difference in the SMSI effect between Pt and Nb_2O_5 or Al_2O_3 [36]. In the reaction of methyl cyclopentane, Pt/Al_2O_3 shows 98% selectivity for hydrogenolysis products, while Pt/Nb_2O_5 gives 71% selectivity for the formation of benzene. The addition of Sn to the catalyst causes a decrease in hydrogenolysis activity, favoring the formation of benzene [37].

For the hydroformylation of ethylene, ethane is a main product in the case of Pd/SiO_2 catalyst, while oxo products (mainly 2-methyl-2-pentanal) become the main products over Pd/Nb_2O_5 [38].

For the ammoxidation of 3-picoline to nicotinonitrile, V_2O_5 (6 wt.%)/Nb_2O_5 has been found to exhibit high conversion (90%) and selectivity (98%) [39]. Nicotinamide, which can be derived by the hydrolysis of nicotinonitrile, is an important chemical compound in the metabolism of human beings and animals and used as a food additive.

Very recently, Cu supported on silica-pillared titanoniobate (Cu/Si–$TiNbO_5$) has been found to show high and relatively stable catalytic activity for the direct decomposition of NO (0.1 vol.% in helium) to N_2 and O_2. The conversions of NO to N_2 and O_2 are 31.5 and 12.5%, respectively, at 650 °C and SV = 3000 cm^3/g h [40]. The change of the conversions with reaction time and no formation of N_2O over the catalyst are different from the case of a well-known Cu-exchanged zeolite catalyst. For the combustion of propane, the conversion of propane is about 35% at 427 °C over both Pd/Al_2O_3 and Pd/Nb_2O_5 catalysts, whereas 100% over Pd/Nb_2O_5/Al_2O_3 [41]. The effect of the support (Nb_2O_5/Al_2O_3) is explained by the presence of Nb_x polymeric structures near to the monolayer which favors the ideal Pd^0/Pd^{2+} surface ratio to propane combustion.

4. Solid acid catalysts

Hydrated niobium pentoxide ($Nb_2O_5{\cdot}nH_2O$) which is called niobic acid has a high acid strength ($H_0 = -5.6$) corresponding to the acid strength of 70% H_2SO_4 when calcined at relatively low temperatures (100–300 °C), though the surface of niobic acid calcined at 500 °C is almost neutral [3,5]. Since any kinds of acidic metal oxides show acidic property on calcination at about 500 °C and the acidic property is lost or decreased by absorbing water, niobic acid which shows high acid strength in spite of its water

Table 7
Activities and selectivities of $Nb_2O_5{\cdot}nH_2O$ and the other solid acids for esterification of ethyl alcohol with acetic acid [42][a]

Catalyst	Reaction temperature (°C)	C_2H_5OH basis		By-products
		Conversion (%)	Ester selectivity (%)	
$Nb_2O_5{\cdot}nH_2O$[b]	120	72	100	
	140	86	100	
Resin[c]	120	38	<99	
	140	50	<98	
$ZrO_2–SO_4{}^{2-}$[d]	140	56	90	$(C_2H_5)_2O$
$Fe_2O_3–SO_2{}^{4-}$[d]	140	13	93	$(C_2H_5)_2O$
$TiO_2–SO_2{}^{4-}$[d]	120	95 (54)[e]	99 (98)[e]	
	140	100	95	C_2H_4
$SiO_2–Al_2O_3$[d]	120	4	99	$(C_2H_5)_2O + C_2H_4$
	140	14	98	$(C_2H_5)_2O + C_2H_4$
HZSM-5[d]	120	82	92	$(C_2H_5)_2O + C_2H_4$
	140	99	72	$(C_2H_5)_2O + C_2H_4$

[a] Catalyst weight: 1 g; volume ratio of acetic acid to ethyl alcohol = 1; reaction time: 1 h.
[b] Calcined at 200 °C.
[c] Calcined at 120 °C.
[d] Calcined at 500 °C.
[e] After 2 h reaction time.

content is an unusual solid acid. The unusual solid acid is known to show high and stable activity for acid-catalyzed reactions in which water molecules participate or are liberated.

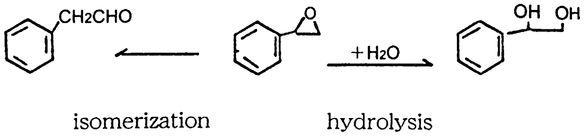
NbPO, which has a higher acid strength of $H_0 = -8.2$ corresponding to the acid strength of 90% H_2SO_4, shows a high catalytic activity for particular reactions. Mixed oxides containing niobium and niobia supported on the other oxides calcined at about 500 °C also show acidic property and catalytic activity. Recently, zeolites, mesoporous materials, and layer compounds containing niobium are known to have acidic property [1,2]. Selected several examples of catalytic application of the solid acids are demonstrated below.

4.1. Esterification

Niobic acid shows high catalytic activity and 100% selectivity for the esterification of ethyl alcohol with acetic acid. As seen in Table 7 [42], one of solid superacids, $TiO_2–SO_4{}^{2-}$ shows a high activity, but the activity rapidly decreases. H-ZSM-5 zeolite also shows a high activity, but forms considerably large amounts of diethyl ether and ethylene as by-products, the selectivity for ester being 92%. Resin becomes black after 1 h reaction so that the repeated use is impossible. However, the activity of niobic acid does not change even after being used for 60 h. For the esterification of acrylic acid with methanol, niobic acid shows 95% conversion of acrylic acid and 100% selectivity, a good stability being observed [43]. Although Nafion-H among various solid acids shows higher activity than niobic acid, it forms a large amount of diethyl ether as a by-product in contrast to niobic acid on which the selectivity for the ester is 100%. Nb_2O_5/SiO_2 calcined at 400 °C shows a low conversion less than 20% for the esterification of acrylic acid with methanol.

4.2. Hydrolysis

The catalytic activity of niobic acid for the hydrolysis of phenyloxirane is remarkable. Phenyloxirane (I) forms phenylacetaldehyde (II) by isomerization and phenyl-1,2-ethanediol (III) by hydrolysis.



(II) (I) (III)

(2)

Table 8
Hydrolysis of phenyloxirane with some solid acid catalysts [44][a]

Catalyst (calcination temperature, °C)	Solvent volume H_2O/dioxanea[b] (ml/ml)	Yield (%)		
		Phenyl-oxirane (I)	Phenyl-acetaldehyde (II)	Phenyl-1,2-ethanediol (III)
Niobic acid (300)	10/90	0.0	11.4	88.6
	50/50	0.0	0.5	99.0
	100/0	0	0	100
SiO_2–Al_2O_3[c] (500)	10/90	3.9	34.8	61.2
SiO_2–Al_2O_3[d] (500)	10/90	8.0	36.4	55.7
H-ZSM-5(500)	10/90	0.3	83.2	16.5
H-silicalite (500)	10/90	63.7	33.8	2.5
H-Nafion	10/90	0.0	25.7	74.3

[a] Reaction time: 3 h; substrate volume: 0.5 ml; catalyst amount: 500 mg; total solvent volume: 100 ml.
[b] Mixture of water and 1,4-dioxane was used as solvent.
[c] High alumina type ($SiO_2/Al_2O_3 = 3$).
[d] Low alumina type ($SiO_2/Al_2O_3 = 6$).

As shown in Table 8, the yield of (III) is higher using niobic acid than those of SiO_2–Al_2O_3, H-ZSM-5, Nafion-H, and H-silicalite in a H_2O/dioxane (10/90) solvent [44]. In particular, the yield is 100% in 100 water of reflux state in the case of niobic acid catalyst. This indicates that niobic acid is not poisoned with water in aqueous solution if the temperature is around 100 °C. This encourages us to apply niobic acid catalyst to the other reactions in aqueous solution. The methanolysis of phenyloxirane also occurs over niobic acid in methanol, the yield being 98% [45].

4.3. Hydration

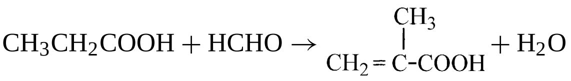
For the hydration of ethylene, the steady-state activity of niobic acid calcined at 300 °C is higher than that of solid phosphoric acid which is widely used in industry [46]. The selectivity for the formation of ethyl alcohol at 200 °C is >97%. Later, the activity of niobic acid was found to be enhanced by treatment with diluted phosphoric acid [47]. The surface acidity of niobic acid treated with phosphoric acid is well maintained up to a high temperature of above 600 °C. This is advantageous for reactivation of used catalyst by high temperature treatment.

For the hydration of propylene, two new solid acids; niobic acid prepared by the pH swing method and Nb_2O_5–ZrO_2 prepared by coprecipitation method, have been reported recently to be active and stable catalysts [48]. For the hydration of cyclohexene to cyclohexanol at 150 °C, a binary oxide, Nb_2O_5–SiO_2, shows 4% conversion (equilibrium value) with 94% selectivity [49]. It is remarkable that niobic acid exhibits the highest catalytic activity among various solid acids such as Amberlist resin, Nafion-H, SiO_2–Al_2O_3, TiO_2–SiO_2, etc. for the hydration of dicyclopentadiene to its hydrate [50].

4.4. Dehydration

NbPO or niobic acid treated with phosphoric acid is effective as a catalyst for the synthesis of methyl-*t*-butyl ether (MTBE), which is useful as a powerful anti-knocking agent, by intermolecular dehydration of *t*-butyl alcohol and methanol [51]. The MTBE yield is much higher than that over TiO_2, ZrO_2, Al_2O_3, SiO_2 or SiO_2–TiO_2 treated with phosphoric acid.

A method of synthesizing methacrylic acid (MAA) from propionic acid (PA) and formaldehyde was reported recently by Spivey [52]:



$$CH_3CH_2COOH + HCHO \rightarrow CH_2{=}\overset{\overset{\displaystyle CH_3}{|}}{C}\text{-}COOH + H_2O \qquad (3)$$

The catalytic activity of Nb_2O_5/SiO_2 for the reaction is much higher than those of Ta_2O_5/SiO_2 and V–Si–P oxide (Table 9). The method may become attractive for MAA production, because PA can be produced economically from ethylene by the following

Table 9
Catalytic activity of Nb_2O_5/SiO_2 for synthesis of MAA from PA and formaldehyde [52][a]

Catalyst	MAA yield (%), HCHO basis	PA basis
Nb_2O_5–SiO_2 (1:4 atom ratio)	71	15.2
Ta_2O_5–SiO_2 (1:4)	26	6.0
V–Si–P (1:10:2.8)	47	10.1

[a] Reaction temperature: 300 °C; pressure: 2 atm.

scheme:

$$C_2H_4 + \frac{CO}{H_2O} \rightarrow CH_3CH_2COOH \qquad (4)$$

Recently, 5-hydroxymethyl-2-furaldehyde (HMF) which is a useful starting material for fine chemicals and polymers has been found to be selectively formed by dehydration of saccharides such as fructose, sucrose, and inuline by using NbPO as a catalyst [53]. For example, HMF forms from fructose over a NbPO catalyst in aqueous solution at 100 °C, the selectivity being 100% at 29% conversion. The NbPO supplied from CBMM which was calcined at 255 °C for 6 h under vacuum is used. The catalytic performance is said to be much better than zirconium phosphate, cation exchange resins, zeolites or supported heteropoly acids. The high selectivity of NbPO will make it possible to produce HMF by recycling the unreacted HMF.

4.5. Condensation

Many patents and papers have been reported on various condensation reactions by use of niobium catalysts such as $Nb_2O_5 \cdot nH_2O$, Nb_2O_5/Al_2O_3, Nb_2O_5/SiO_2, and $NbOPO_4$ [1–4].

One of the most interesting reactions is Prins reaction. The reaction of isobutyraldehyde (IBA) with isobutene (IB) forms various products such as 2,5-dimethyl-2,4-hexadiene (OCD), double bond positions isomers (i-OCD), isobutyl alcohol (IBOH), isobutyl isobutyrate (IBIB), isobutyric acid (IBUA), and olefin oligomers, the structural formulas of the reactants and products being given in Fig. 6 [54]. Among these products, OCD is an important intermediate in the synthesis of agricultural drugs. As shown in Fig. 7, niobic acid (CBMM product) gives the best yield of OCD at reaction temperature of 254 °C [54]. A comparison of the catalytic activity and selectivity of niobic acid with those of 16 wt.% H_2SO_4 is given in Table 10 [55]. A solid acid, niobic acid, shows much higher selectivity than a liquid acid, 16 wt.% H_2SO_4. The process using niobic acid catalyst has been commercialized by Sumitomo Chem. for more than 10 years.

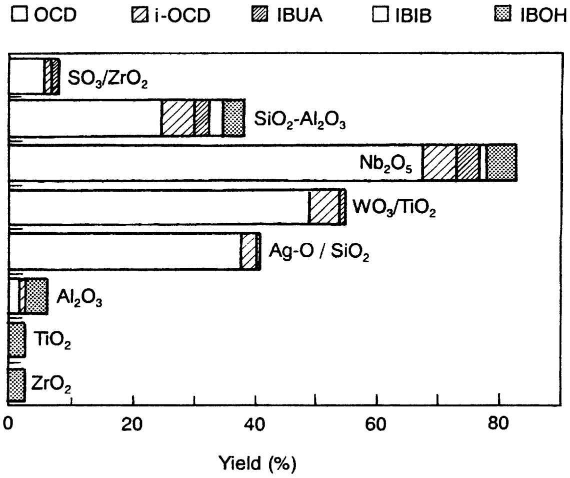


Fig. 7. Product yields in reaction of IBA with IB over various catalysts. Reaction temperature, 252 °C; catalyst amount, 0.5 g; flow rate of olefin and aldehyde, 2150 and 230 ml STP/h, respectively [54].

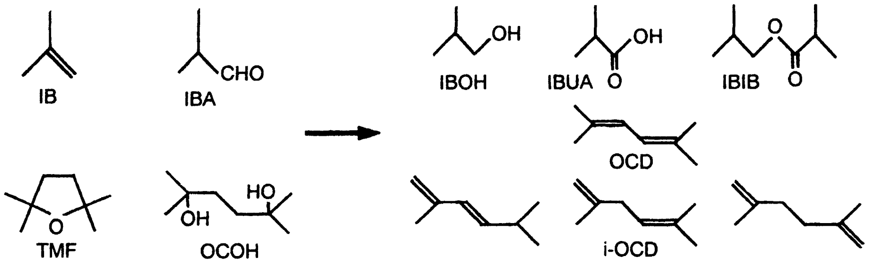


Fig. 6. Structural formula of reactants and products. See text for abbreviated symbols [54].

Table 10
Comparison of catalytic performance of niobic acid with that of sulfuric acid for synthesis of OCD from IBA and IB at 200 °C [55]

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

Recently, niobium pentoxide calcined in the range of 400–900 °C has been reported to be active for gas phase aldol condensation of acetone at 250 °C [56]. A main product is mesitylene over the niobia calcined at 400 °C, while it is mesityl oxide over the niobia calcined at 500–900 °C. The change in selectivity is ascribed to be due to Brönsted acid sites in the former niobia and Lewis acid sites in the latter niobia. Since both Brönsted and Lewis acidity of niobic acid is known to greatly decrease when calcined at above 400 °C [32,57], the above results are interesting. However, the appearance of the catalytic activity of niobia calcined at above 400 °C is considered mainly due to relatively high reaction temperature employed.

4.6. Alkylation

Various alkylation reactions using niobic acid, NbPO, niobic acid treated with phosphoric acid, Nb_2O_5–ZrO_2, etc. as catalysts were already reviewed in 1995 [1]. After that, the benzylation of anisol with benzyl alcohol in liquid phase at 150 °C has been reported to take place over niobic acid calcined at 300 °C, the conversion of alcohol and the selectivity for benzylation products being 79 and 63%, respectively [58].

5. Photocatalyst

It was found by Domen et al. [59] that water is decomposed to give hydrogen and oxygen in the presence of a Ni–$K_4Nb_6O_{17}$ catalyst under UV irradiation. A catalyst with the layered structure of potassium niobate containing ultrafine particles of nickel metal in the interlayer spaces shows a stable and high photocatalytic activity for water decomposition.

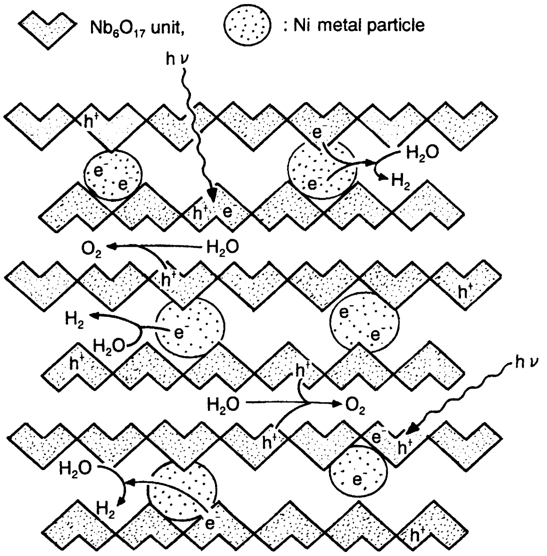


Fig. 8. Schematic structure of the active Ni-loaded $K_4Nb_6O_{17}$ photocatalyst and the reaction mechanism of H_2O decomposition into H_2 and O_2 [60].

The mechanism of H_2 and O_2 evolution from H_2O is shown in Fig. 8 [60], where H_2 and O_2 form separately in the interlayers I and II, respectively. Since the catalyst is reduced with hydrogen at 500 °C and oxidized at 200 °C before use, the nickel attached to outer surfaces of $K_4Nb_6O_{17}$ is oxidized and therefore it does not catalyze the recombination of H_2 and O_2. However, the above treatment of the catalyst does not oxidize the nickel metal formed by reduction in the interlayer I. This is the reason why this catalyst is highly active and stable. The mechanism is entirely different from that observed on conventional photocatalysts such as Pt/TiO_2.

High quantum yields of about 10% for the decomposition of water are obtained over $K_4Nb_6O_{17}$ or $Rb_4Nb_6O_{17}$ combined with Ni or Pt. A layered perovskite compound (H^+-exchanged $K_{0.5}La_{0.5}Ca_{1.5}Nb_3O_{10}$) was also reported to show a photocatalytic activity. The rate of H_2 evolution is 2030 μmol h^{-1} over the compound and 13,500 μmol h^{-1} over the compound combined with Pt [61]. Recently, Cs as a metal combined with potassium niobate has been reported to show higher photocatalytic activity than Pt, Ni, Ru, etc. for the hydrogen evolution, where formaldehyde and formic acid as additives to water accelerate the rates of hydrogen and oxygen, respectively [62].

Titania has a potential use in the photocatalytic destruction of organic wastes. The addition of a small amount of Nb_2O_5 to TiO_2 powder is reported to significantly increase surface acidity and photocatalytic activity [63].

6. Conclusion

Interesting and important examples of catalytic application of niobium compounds and materials reported up to 2001 have been demonstrated.

The promoter effect and the support effect of niobium on catalytic performances for diversified reactions are really surprising, where redox property and acidic property of niobium compounds play important roles. The characteristic features of niobic acid, NbPO, and mixed oxides containing niobium as solid acid catalysts and niobium compounds having layered structures as photocatalysts are striking and intriguing.

Further catalytic applications of these kinds are expected to improve existing catalytic processes and establish new processes in near future. In particular, niobium compounds as unusual solid acid catalysts will be promising for production of fine chemicals by much less cost and environmentally safer processes.

For further details of preparation methods of niobium compounds, characterization of surface properties (active sites, etc.), and reaction mechanism, which are not fully described here because of limited spaces, it would be useful to refer to the references cited in this paper and the special issues of niobium in Catalysis Today: vol. 8, No. 1 (editor: E. Ko), 1990; vol. 16, Nos. 3–4 (editor: K. Tanabe), 1993; vol. 28, Nos. 1–2 (editor: K. Tanabe), 1996; vol. 57, Nos. 3–4 (editors: M. Schmal, et al.), 2000.

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