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Recent topics of research and development of catalysis by niobium and tantalum oxides

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Abstract

Current topics of catalysts containing niobium and tantalum, especially in the field of solid acid catalysis and selective oxidation of hydrocarbons are reviewed. Hydrated niobium oxide and hydrated tantalum oxide are highly acidic. Hydrated niobium oxide is active for the hydration of ethene to ethanol, and Nb–W mixed metal oxide is more active for the reaction. Acid properties of tantalum oxide are changed by being supported on SiO_2. Ta oxide/SiO_2, prepared by the chemical reaction between tantalum alkoxide and surface hydroxyl groups of SiO_2, is active and selective for the gas phase Beckmann rearrangement of cyclohexanoneoxime to caprolactam. Niobium oxide and tantalum oxide easily react with many other oxides to form mixed metal oxide phases with complex structure. Mixed metal oxide catalysts, containing molybdenum, vanadium, certain elements together with niobium are active for the selective oxidation of hydrocarbons. Especially, the selective oxidation of propane by such mixed metal oxide catalysts has been paid attention. Additionally, recent progress of environmental catalysts, promoted by niobium and tantalum compounds, namely catalysts for the pollution abatement is reviewed. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: Niobium oxide; Tantalum oxide; Solid acid; Selective oxidation; Ammoxidation; Environmental catalysts

1. Introduction

Although niobium and tantalum were not attracted attentions as a catalyst component until the early in the 1960s, many catalytic applications of the elements were reported during 1970s and 1980s. Niobium oxide and tantalum oxide have been reported to remarkably enhance catalytic activity and selectivity and to prolong catalyst life when a small amount of the oxides was added to known catalysts. Niobium oxide is well known to exhibit a pronounced effect as a support for metal and metal oxide catalysts. As niobium oxide and tantalum oxide easily react with many other oxides to form mixed metal oxide phases with complex structure, a lot of mixed metal oxides containing niobium or tantalum have been researched, especially in the field of selective oxidation of hydrocarbons. Furthermore, niobium oxide and tantalum oxide are highly acidic, especially in an amorphous form. Hence, a lot of applications of the oxides for industrial catalysts have been expected.

In this paper, I would like to present the current topics of catalysts containing niobium and tantalum, especially in the field of solid acid catalysis and the selective oxidation of hydrocarbons. Additionally, recent progress of environmental catalysts, promoted by niobium and tantalum compounds, namely catalysts for the pollution abatement is reviewed.

2. Solid acid catalysis

Hydrated niobium oxide ($Nb_2O_5{\cdot}nH_2O$) and hydrated tantalum oxide ($Ta_2O_5{\cdot}nH_2O$) are highly acidic.

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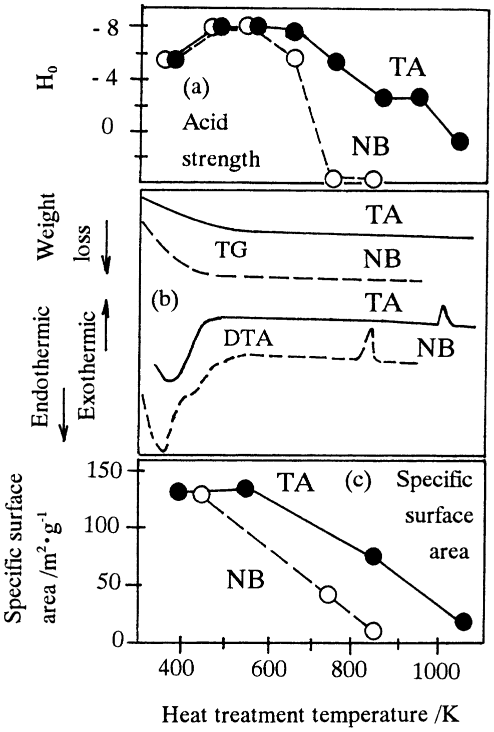

Fig. 1. (a) Acid strength, (b) TG–DTA analyses and (c) specific surface area of hydrated niobium oxide (NB) and hydrated tantalum oxide (TA).

Fig. 1 shows (a) acid strength, (b) TG–DTA curves and (c) specific surface area of these hydrated oxides, heat treated at different temperatures [1]. The H_0 value, measured by Hammett indicators, of these hydrated oxides is less than −8.2, equal to about 90% sulfuric acid. The acid strength of these hydrated oxides changes upon heat treatment. The acid strength begins to decrease, if the temperature goes beyond appropriate points: around 700 K for hydrated tantalum oxide and 600 K for hydrated niobium oxide. Upon heat treatment at the higher temperature, the acid property is weakened, and the specific surface area drastically decreases. In the DTA analysis of hydrated tantalum oxide, an exothermic peak appears at about 1003 K, without weight loss. With hydrated niobium oxide, however, the exothermic peak appears at the lower temperature, namely about 853 K. These exothermic peaks are due to their crystallization, which was confirmed by the X-ray diffraction method.

Hydrated niobium oxide was reported to be active for the gas phase hydration of ethene to ethanol [2]. Asaoka and co-workers [3] demonstrated that the particle diameter and the populations of surface acid sites of hydrated niobium oxide were important for the activity and the life of the catalysts. In the concrete, the proper mean particle diameter might be larger than 1000 nm, and the proper amount of acid sites with $H_0 \leq -3.0$ might be 0.35 mmol g^{-1}. Furthermore, they suggested that the H_0 value of more than 50% of the acid sites should be less than −5.6, as shown in Table 1. The preparation conditions seem to be important to obtain such efficient hydrated niobium oxide. Although hydrated niobium oxide is active for the hydration of ethene, Nb–W mixed metal oxide with wide range of Nb/W atomic ratio is more active, as shown in Fig. 2 and has long catalyst life [4]. However, new crystal phases are not detected for the Nb–W mixed metal oxide catalysts, and the active site has not been clear yet.

Acid properties of tantalum oxide are changed by being supported on SiO_2. Ta oxide/SiO_2, prepared by the chemical reaction between tantalum alkoxide and surface hydroxyl groups of SiO_2, is active and selective for the gas phase Beckmann rearrangement of cyclohexanoneoxime to caprolactam, as shown in Table 2 [5]. Highly dispersed tantalum oxide species

Table 1
Effect of mean particle diameter and acid amount of hydrated niobium oxide catalysts on the activity of hydration of ethene[a]

Mean particle diameter (nm)	Acid amount (mmol g^{-1})		Ethene conversion (%)	Selectivity[b] (%)
	$H_0 \leq -3.0$	$H_0 \leq -5.6$		
3000	0.55	0.50	1.21	≥99
3000	0.41	0.30	0.70	≥99
800	0.30	0.27	0.52	≥99

[a] Reaction conditions: pressure=3 MPa, GHSV=1500 h^{-1}, temperature=553 K, catalyst amount=10 cm^3, H_2O/C_2H_4=1 mol mol^{-1}.
[b] Selectivity for (ethanol+ethyl ether).

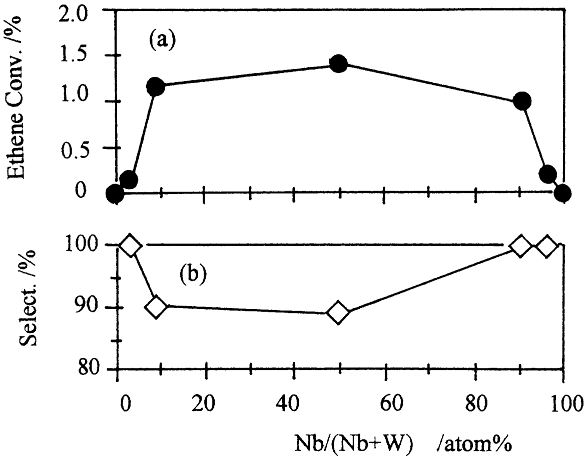

Fig. 2. (a) Conversion of ethene and (b) selectivity for (ethanol+ethyl ether) of Nb–W mixed metal oxide catalysts.

were formed on the surface by controlling the preparation conditions, such as type of alkoxy group of tantalum alkoxide, concentration of alkoxide in the solution, and impregnation temperature, confirmed by SEM, EPMA and XAFS analyses. Acid properties of tantalum oxide seem to be changed by the symmetry and oxidation state of metal cation (Ta^{m+}).

Recently, several patents and papers were reported concerning the application of hydrated niobium oxide as catalysts for the fine chemical synthesis such as the syntheses of 2,5-dimethyl-2,4-hexadiene, an intermediate substance of an agricultural drug [6] and β-cyanopropionamide from succinonitrile [7].

3. Selective oxidation

Selective oxidation of hydrocarbons, particularly propene, butenes, xylenes and so on, are industrially important. Niobium oxide and tantalum oxide are effective promoters for the improvement of activity and selectivity of such oxidation catalysts, for examples, propene to acrolein, isobutene to methacrolein and isobutene to methacrylonitrile. $Mo_{12}Bi_9Nb_3O_x$ multicomponent mixed metal oxide catalyst was reported to be more active and more selective for the oxidation of isobutene to methacrolein than Mo–Bi and Mo–Nb binary mixed metal oxide catalysts [8]. Furthermore, niobium oxide was reported to enhance the activities of V_2O_5–Sb_2O_3–P_2O_5–TiO_2 mixed metal oxide catalyst for the selective oxidation of *o*-xylene to phthalic anhydride and the ammoxidation of aromatic methyl group [9].

A lot of mixed metal oxides containing niobium or tantalum have been reported, because niobium oxide and tantalum oxide easily react with many other oxides to form mixed metal oxide phases with complex structure. However, the role of niobium or tantalum as a promoter has not been clear in many cases. Thorsteinson et al. [10] demonstrated that Mo–V–Nb mixed metal oxide catalysts were effective for the oxidative dehydrogenation of ethane to ethene. Mixed metal oxide catalysts, containing molybdenum and vanadium together with niobium are active as low as 473 K for the reaction, as shown in Table 3. The presence of niobium seems to stabilize the catalyst structure against oxidation and reduction and to permit a very strongly oxidized or reduced catalyst to be returned more readily to its original state. The excellent Mo–V–Nb catalysts are characterized by a broad X-ray diffraction band near 0.4 nm.

The lower price of alkane relative to alkene has since long provided an incentive for the development of a process for the selective oxidation of alkane to industrially important chemicals. For example, several catalysts have been reported for the direct ammoxidation

Table 2
Catalytic activities of silica-supported tantalum oxides for the vapor phase Beckmann rearrangement of cyclohexanoneoxime, compared with the other solid acid catalysts[a]

Catalyst	Oxime conversion (%)	Caprolactam selectivity (%)
Ta_2O_5 4.3 wt.%/SiO_2	96.5	97.5
B_2O_3 26.5 wt.%/SiO_2	93.4	92.1
H-mordenite	42.5	63.4
$Ta_2O_5 \cdot nH_2O$	42.6	69.9
$Nb_2O_5 \cdot nH_2O$	21.2	67.5

[a] Temperature=573 K, GHSV=4800 h^{-1}, oxime/benzene/N_2=4/42/54 mol% (mol).

Table 3
Activity and selectivity of mixed metal oxide catalysts for the oxidative dehydrogenation of ethane[a]

Catalyst (mixed metal oxide composition)	Temperature for 10% conversion, T_{10} (K)	Selectivity to C_2H_4 at T_{10} (%)
$Mo_{0.8}V_{0.2}$	813	100
$Mo_{0.8}Nb_{0.2}$	907	74
$Mo_{0.73}V_{0.18}Nb_{0.09}$	559	100
$Mo_{0.76}V_{0.19}Fe_{0.05}$	708	87
$Mo_{0.67}V_{0.17}Mn_{0.17}$	778	100

[a] Reaction conditions: $C_2H_6/O_2/N_2$=9/6/85 mol%, GHSV=340 h^{-1}.

of propane to acrylonitrile (ACN), which is an intermediate for the preparation of fibers, synthetic resins, synthetic rubbers, etc. V–Sb mixed metal oxide catalysts have been widely studied for the ammoxidation of propane. Bradzil et al. [11] applied lots of patents and studied the reaction mechanism. The performance of V–Sb oxides is enhanced by doping with different metal ions, such as Nb, W, Mg, Te, Ga, Pb and Sm [12]. These metal ions seem to affect the surface acidic and bulk redox properties and on the catalytic performance. Miura et al. [13] reported that Sb–Nb–V mixed metal oxides were active and selective for the ammoxidation of propane. Although the catalytic activity of $SbNbO_4$ being isostructural to α-Sb_2O_4 was very low, $SbNbO_4$ containing V^{4+} dissolved in the solid solution showed an increased catalytic activity and selectivity for ACN, as shown in Table 4. The authors demonstrated that the ammoxidation of propane was carried out on the cleavage of the [0 1 0] plane that was constructed with coordination-unsaturated Nb^{5+} ions and doubled bond oxygen ions combined with Sb^{5+} ions created by the substitution of V^{4+} ions for Nb^{5+} ions.

The other mixed metal oxide catalysts containing Nb or Ta have been reported for the selective (amm)oxidation of propane and isobutane. For example, Nb–Sb–Cr oxide [14], Ca–Bi–Nb–Mo oxide [15], Cr–Sb–W–Nb oxide [16], Mo–Sb–W–Nb oxide [17] were demonstrated to be effective for the ammoxidation of propane to acrylonitrile, and Matsuura et al. suggested that tantalum oxide and niobium oxide significantly enhanced the activation of propane and isobutane, that appeared in Ta–W–Li–Ce–Mo oxide and Nb–W–Li–Ce–Mo oxide [18] and Nb–Bi–Mo oxide catalysts [19].

We have reported that mixed metal oxides comprising molybdenum, vanadium, niobium and tellurium are highly active and selective for the ammoxidation of propane to acrylonitrile [20]. Table 5 shows that the combination of these four elements seems to be necessary for high efficiency of ACN synthesis. Mo–V–Nb–Te mixed metal oxide activates both of propane and ammonia at relatively low temperatures, compared with V–Sb and Mo–Bi mixed metal oxides [21]. There are at least two crystal phases participating the elementary steps of the ammoxidation of propane

Table 4
Activities and selectivities of Sb–Nb–V oxide catalysts for the ammoxidation of propane[a]

Catalyst Sb:Nb:V atomic ratio	C_3H_8 conversion (%)	Selectivity (%)		Crystal phase present[b]
		Acrylonitrile	C_3H_6	
1:1:0	4.2	6.7	76.0	$SbNbO_4$
1:0.95:0.05	24.5	34.5	37.9	$SbNbO_4$
1:0.9:0.1	30.6	42.2	38.0	$SbNbO_4$
1:0.8:0.2	28.8	40.5	42.6	$SbNbO_4$+$SbVO_4$ (trace)
1:0.5:0.5	24.7	38.8	40.9	$SbNbO_4$+$SbVO_4$
1:0.2:0.8	22.5	34.5	41.9	$SbNbO_4$+$SbVO_4$
1:0:1	19.4	17.6	36.6	$SbVO_4$

[a] Reaction conditions: catalyst amount=5 g, reactant flow rate=40 cm^3 min^{-1}, $C_3H_8/NH_3/O_2/He$=1/1/2/2 mol.
[b] Crystal phases were determined by the X-ray diffraction method.

Table 5
Catalytic activities of Mo–V–X–Y oxides for the ammoxidation of propane[a]

Catalyst	Reaction temperature (K)	Conversion of propane (%)	Selectivity for ACN (%)
$Mo_1V_{0.4}Nb_{0.1}Te_{0.2}O_x$	693	62.0	63.0
$Mo_1V_{0.4}Te_{0.2}O_x$	693	14.5	24.1
$Mo_1V_{0.4}Nb_{0.1}O_x$	693	34.2	10.5
$Mo_1Nb_{0.1}Te_{0.2}O_x$	703	0	–
$V_{0.4}Nb_{0.1}Te_{0.2}O_x$	703	0.6	–

[a] Catalyst amount=0.5 cm^3, GHSV=500 h^{-1}, $C_3H_8/NH_3/O_2/N_2$=1/1.2/2/8 (mol).

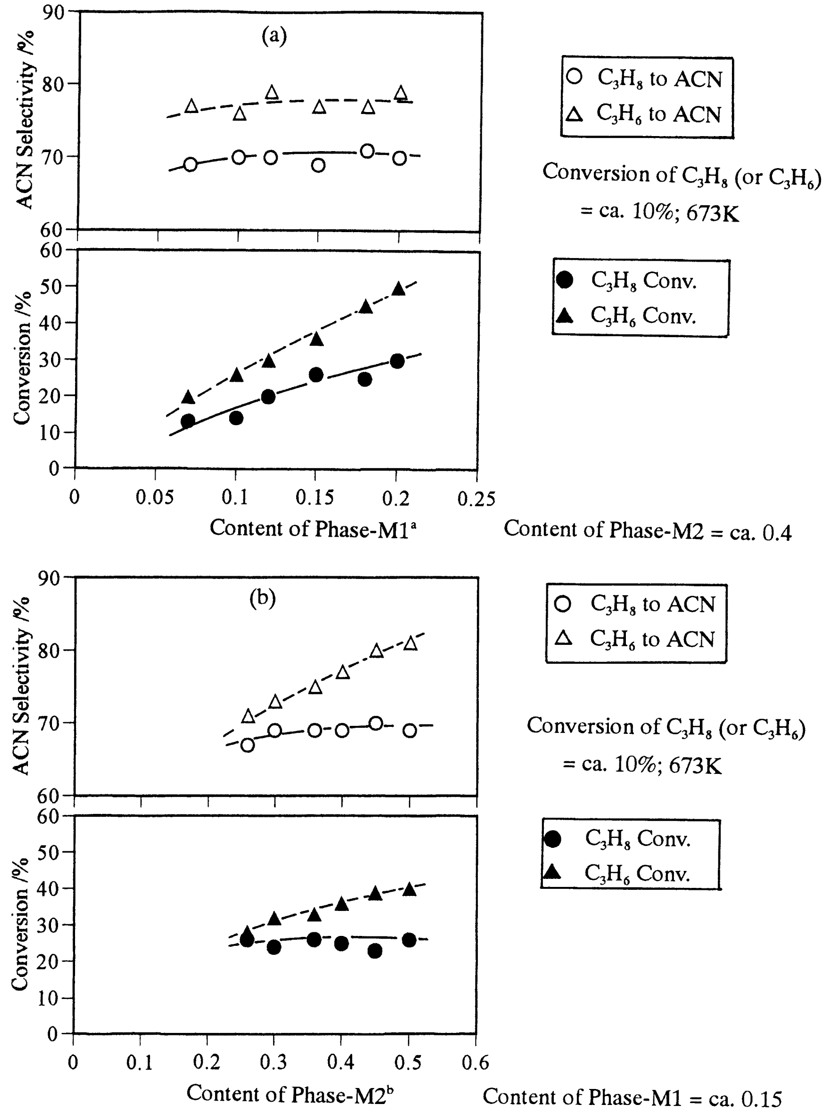

Fig. 3. Effect of contents of (a) Phase-M1 and (b) Phase-M2 on conversion of propane and selectivity for ACN over Mo–V–Nb–Te mixed metal oxide catalysts.

[22]. X-ray diffraction measurement with an internal standard shows that one crystal phase is effective for the activation of propane and that the other one is effective for the formation of ACN from propane and propene, that is shown in Fig. 3. The structure and the role of these crystal phases are under investigation.

4. Environmental catalysts

There have been a lot of papers and patents concerning the catalysts for the pollution abatement. Tanabe [23] reviewed the progress of the catalysts for SCR (selective catalytic reduction) of NO_x by NH_3 as a reducing agent in the industrial stack gas. The addition of niobium oxide to V_2O_5–TiO_2, that is the most popular catalyst for this process, was found to be effective to improve the low temperature SCR activity. The addition of Nb is also effective for stabilizing the catalyst and for improving its mechanical strength. Surface niobium oxide phase, formed by the reaction with TiO_2 support, seems to exhibit a pronounced effect on the physical and chemical properties of these oxide supports. Furthermore, the surface oxide phases impart thermal stability to the oxide supports at elevated temperatures by retarding the loss of surface area. Such promoted catalysts are expected to be applied to the removal of dioxines in the exhaust gas from the incinerators.

Table 6

Reduction of NO to N_2 and O_2 over amorphous Ni–Ta–Pd alloy/Al_2O_3 catalyst[a]

Temperature (K)	Conversion (%)
873	26
973	48
1073	64
1173	75

[a] Catalyst: Pd 3 wt.%, Ni 50 at.%, Ta 34 at.%, Pd 16 at.%/Al_2O_3. Reaction conditions: catalyst amount=1 g, NO 5000 ppm/He, 30 ml/min.

Table 7

Reduction of NO to N_2 and O_2 over amorphous alloy/Al_2O_3 catalyst[a]

Catalyst (at.%)	Conversion (%)
50 Ni-20 Ta-10 Pd	70
50 Ni-20 Ta-20 Pd	78
50 Ni-20 Ta-40 Pd	90
50 Ni-1 Co-20 Ta-40 Pd	90
50 Ni-1 Co-30 Ta-40 Pd	81
50 Ni-10 Nb-40 Pd	71
50 Ni-1 Ta-10 Nb-40 Pd	71

[a] Reaction conditions: catalyst amount=1 g, NO 5000 ppm/He, 30 ml/min, temperature=1173 K.

SCR process for the removal of NO_x by NH_3, CO and hydrocarbons is widely carried out in the industrial stack gas. However, it is difficult to apply SCR process for the removal of NO_x in the exhausts of lean–burn

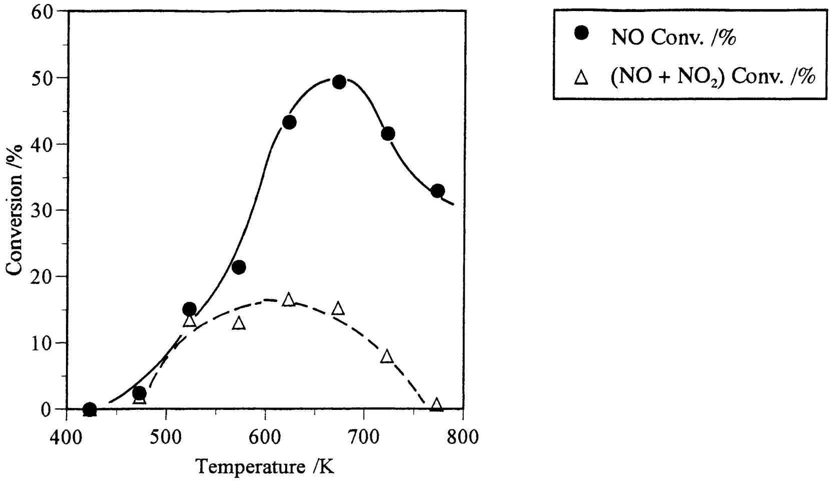

Fig. 4. Catalytic activity of Nb (5 at.%)–Cu (5 at.%)/Al_2O_3 catalyst for the decomposition of ($NO+NO_2$) mixture.

Table 8
Removal of C_6H_{14} over Pd/Nb_2O_5 catalyst, compared with Pd/Al_2O_3 catalyst[a]

Catalyst	Temperature (C_6H_{14} conversion=50%) (K)	SO_2 conversion[b] (%)
Pd 2 wt.%/Nb_2O_5	628	10
Pd 2 wt.%/Al_2O_3	663	55

[a] Reactant composition: C_6H_{14}=600 ppm, SO_2=50 ppm, O_2=10 vol.%, CO=5 vol.%, CO_2=1000 ppm, NO=300 ppm, H_2O=10 vol.%, N_2=balance.

[b] Temperature=673 K.

spark and automobile with diesel engine because the catalysts for SCR process are significantly deactivated under the conditions. Concretely, the partial pressure of oxygen is high, and the temperature is low. Furthermore, there are a considerable amount of SO_x and particles existing in the exhaust from diesel engines. The direct decomposition of NO_x to N_2 and O_2 is thermodynamically favorable at the lower temperatures. Hashimoto et al. [24] reported that amorphous Ni–Ta–Pd alloy supported on Al_2O_3 with high surface area is active for the direct decomposition of NO_x, as shown in Table 6. Table 7 shows that Ni–Co–Ta–Pd alloy supported on Al_2O_3 and Ni–Nb–Pd alloy supported on Al_2O_3 are also active for the reaction. The oxidation state of Ta or Nb of such catalysts is not clear.

Recently, Balt [25] demonstrated that niobium oxide supported on alumina promoted by Cu, Zn, Ga, Sn or In is active for the removal of NO_x by the reaction between NO_x and hydrocarbons in the diesel exhaust. Tantalum oxide supported on Al_2O_3 promoted by the same elements is also active for the reaction. The typical catalytic activities are shown in Fig. 4. These niobium oxide and tantalum oxide catalysts are effective for the removal of NO_x under the high oxygen partial pressure.

There is a considerable amount of SO_2 in the industrial stack gas. The efficiency of NH_3 as a reducing agent on the removal of NO_x decreases because NH_3 reacts with SO_3, that is formed by the oxidation of SO_2. Hence, it is preferable that the oxidation of SO_2 is prevented. $(VO)_2(SO_4)_3/SiO_2$ catalyst promoted by Nb_2O_5 is effective for the suppression of oxidation of SO_2 under the conditions of NO_x removal [26]. Pd supported on Nb_2O_5 and Pd supported on Ta_2O_5 catalysts were reported to be effective for the suppression of oxidation of SO_2 during the removal of hydrocarbons of diesel exhaust, as shown in Table 8, [27].

Recently, the simultaneous removal of NO_x and poisonous organic chlorine compounds has interested the world. Baba et al. [28] reported that Ti–W–Nb–V oxide catalysts were effective for the reaction in the long period.

Catalytic applications of niobium oxide and tantalum oxide will be expected to be extended in the future.

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