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Activation of propane and butanes over niobium- and tantalum-based oxide catalysts

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Abstract

Niobium and tantalum are important elements for the activation of alkanes in the viewpoints of acidic property and the formation of unique mixed metal oxides. And the difference of the ability of alkane activation between niobium- and tantalum-based oxide catalysts is studied. Although hydrated niobium and tantalum oxides show strong acid property, only hydrated tantalum oxide is activated to a solid superacid by the treatment with sulfuric acid, and isomerizes *n*-butane to isobutane at room temperature. The sulfuric acid treated tantalum oxide activates P–Mo–V heteropolyacid compounds for the selective oxidation of isobutane to methacrolein (MAL) and methacrylic acid (MAA). The difference of ability of alkanes activation between niobium and tantalum is studied by using surface science technique. Mo–V–Nb–Te mixed metal oxide catalysts are active for the ammoxidation of propane to acrylonitrile (AN). However, Mo–V–Ta–Te mixed metal oxide is less active. The effect of catalyst preparation condition is studied. Mo–V–Nb–Te mixed metal oxide catalysts are also active for the oxidation of propane to acrylic acid (AA).

Keywords: Tantalum-based; Ammoxidation; Heteropolyacid

1. Introduction

Selective catalytic oxidation of alkanes has been attracted much attention from both the industrial and fundamental point of view because alkanes are less expensive but more difficult to functionalize. Maleic anhydride has been already commercially produced by the selective oxidation of *n*-butane. Recently, several catalysts and processes for selective one-stage syntheses of acrylonitrile (AN) and acrylic acid (AA), important and versatile chemical intermediates for fibers and plastics, from propane have been reported [1–9]. Also, the selective oxidation of isobutane to methacrylic acid (MAA) has been studied.

The activation of alkanes, that is the first step of selective oxidation, is an energetically uneasy step. Several fundamental mechanisms have been demonstrated for the activation of alkanes including the oxidative mechanism, the hydride ion abstraction on the acid site, the activation on the basic site via epoxide and so on.

There have been a lot of papers and patents that niobium- and tantalum-based oxide catalysts are effective for the selective oxidation of alkanes. In this paper, I wish to report that niobium and tantalum are important elements for the activation of alkanes in the viewpoints of acidic property and the formation of unique mixed metal oxides. Furthermore, the difference of the ability of alkane activation between niobium- and tantalum-based oxide catalysts is considered, although

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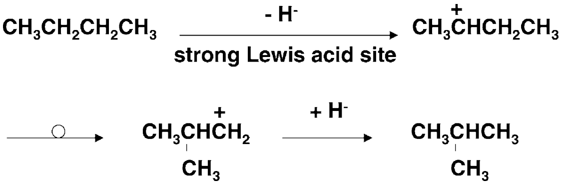
the physical properties and structure of these oxides are similar.

2. Activation of butanes over tantalum-based oxide catalysts

Strong acid sites of the metal oxide catalysts are effective to abstract H^- ion from alkane molecules to form carbenium cations that are the intermediates to dehydrogenated molecules and oxygenated molecules. Previously, we reported that hydrated niobium and tantalum oxides are highly acidic in an amorphous form [10]. However, the strong acid property of hydrated tantalum oxide was maintained to higher temperatures than that of hydrated niobium oxide. And hydrated tantalum oxide showed mainly Lewis acidity in the absence of water, that was confirmed by infrared spectroscopy and the isomerization of 1-butene.

The acid property of hydrated tantalum oxide was promoted by the treatment with sulfuric acid. The treatment of hydrated tantalum and niobium oxides with sulfuric acid is written in the previous paper [10]. The acid strength (H_0) of the hydrated tantalum oxide treated with sulfuric acid (H_2SO_4/TA) was less than −13.75, measured by the color change of 2,4-dinitrotoluene.

H_2SO_4/TA catalyzed the isomerization of *n*-butane at room temperature, as shown in Table 1. The selectivity for isobutane was at least 95%, and the selectivities for methane, ethane and propane were very low in the isomerization. Furthermore, hydrogen was not detected. These results suggest that the isomerization of *n*-butane started through the abstraction of H^- ion by the strong Lewis acid site of the catalyst. The mechanism is different from the isomerization over strong Brønsted acid site, that was suggested to occur via carbonium ions over HY zeolites [11] and SbF_5–SiO_2–Al_2O_3 [12]. Over H_2SO_4/TA catalyst, the subsequent rearrangement of the carbenium ion, followed by the recombination with hydrogen, produces isobutane as shown in Scheme 1. Hydrated tantalum oxide itself was substantially inactive for the isomerization of *n*-butane. Hydrated niobium oxide was not activated by the treatment with sulfuric acid.



Scheme 1. Mechanism of the isomerization of *n*-butane over H_2SO_4/TA catalyst.

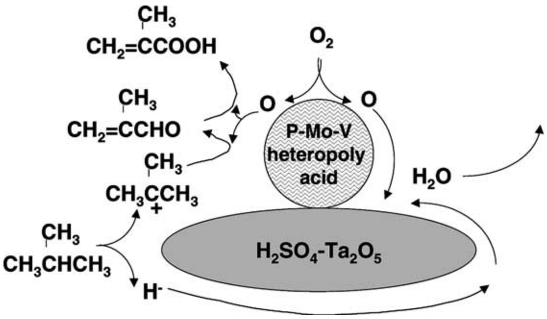
The hydrated tantalum oxide treated with sulfuric acid (H_2SO_4/TA) activated P–Mo–V heteropolyacid compounds for the selective oxidation of isobutane to methacrolein (MAL) and MAA, as shown in Table 2. P–Mo–V heteropolyacid compounds are known to be active for the oxidation of isobutene to MAL and MAA. The combination of the strong acid component (H_2SO_4/TA) and the selective oxidation component (P–Mo–V heteropolyacid compounds) for the olefinic compounds is effective for the selective oxidation of isobutane to MAL and MAA. The mechanism is assumed in Scheme 2. The strong acid site on the hydrated tantalum oxide treated with sulfuric

Table 1
Isomerization of *n*-butane to isobutane over the hydrated tantalum oxide treated with sulfuric acid[a]

Catalyst	Yield (%)	
	Isobutane	*n*-Butane
$H_2SO_4/Ta_2O_5 \cdot nH_2O$[b]	9.6	90.1
$Ta_2O_5 \cdot nH_2O$	0	100
$H_2SO_4/Nb_2O_5 \cdot nH_2O$	0	100
$Nb_2O_5 \cdot nH_2O$	0	100

[a] Reaction conditions: temperature = 293 K, reaction time = 100 h, pressure of *n*-butane = 4×10^4 Pa, catalyst amount = 1 ml.

[b] Small amounts (<0.3 mol%) of methane, ethane and propane were detected.



Scheme 2. Mechanism of the oxidation of isobutane over P–Mo–V heteropolyacid supported on Ta_2O_5, treated with sulfuric acid.

Table 2
Oxidation of isobutane to MAL and MAA[a]

Catalyst	Isobutane conversion (%)	Yield (%)	
		MAL	MAA
$P_1Mo_{11}V_1O_x$ (50 wt.%)/H_2SO_4–$Ta_2O_5 \cdot nH_2O$	28.5	3.8	11.7
$P_1Mo_{10}V_2O_x$ (50 wt.%)/H_2SO_4–$Ta_2O_5 \cdot nH_2O$	27.5	3.5	11.7
$P_1Mo_{11}V_1O_x$ (50 wt.%)/$Ta_2O_5 \cdot nH_2O$	8.7	1.0	3.5
$P_1Mo_{11}V_1O_x$ (50 wt.%)/diatomaceous earth	7.9	1.1	3.6

[a] Reaction conditions: GHSV = 1800, temperature = 623 K, isobutane/O_2/N_2 = 4/8/88 mol%.

acid seems to abstract H^- ion from isobutane and to form $i\text{-}C_4H_9^+$. The $i\text{-}C_4H_9^+$ might migrate to the P–Mo–V heteropoly acid and be oxidized to MAL and MAA. However, the hydrated tantalum oxide without the treatment with sulfuric acid was less active for the selective oxidation of isobutane, because the activation of isobutane was not effectively carried out over the hydrated tantalum oxide without the treatment.

Previously, we prepared the ordered niobium oxides thin film on Pt(1 1 1) and their defect face by using UHV surface analysis apparatus in order to clarify the origin of the acid property of niobium oxide [13–15]. The oxygen vacancies of niobium oxide on Pt(1 1 1) were created by Ar^+ ion bombardment. And the measurement of adsorption of H_2O, CH_3OH and ethene on these model surface oxide layer was studied. H_2O and CH_3OH exhibit associated adsorption on the ordered NbO_x and Nb_2O_5 surface, and dissociative adsorption on the defect Nb_2O_5 surface at room temperature. On the ordered NbO_x and Nb_2O_5 surface, no evidence of ethene adsorption at 200 K is found by HREELS, although ethene adsorbs molecularly on the defect Nb_2O_5 surface with a π-complex formation. These results imply that oxygen vacancies of NbO_x surface play an important role on the adsorption of the molecules and that the defect structure is related to the origin of acidic property of niobium oxide. However, *n*-butane did not adsorb on the defect face of niobium oxide at room temperature.

On the other hand, it was observed that *n*-butane adsorbed dissociatively on the defect face of tantalum oxide on Pt(1 1 1), similarly prepared as niobium oxide layer on Pt(1 1 1), as shown in Fig. 1, at room temperature. Higher temperature than 1200 K is necessary

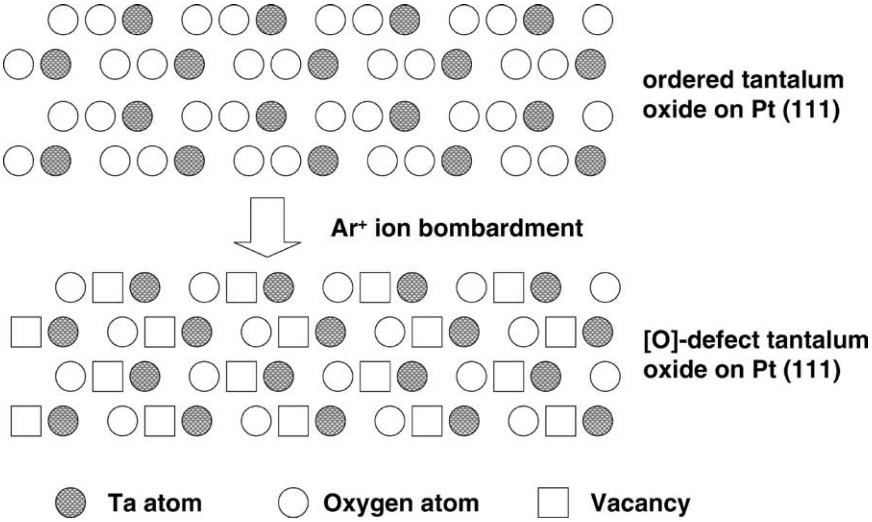


Fig. 1. Surface model oxide of Ta with well-defined structure on Pt(1 1 1).

for the preparation of the well-defined surface tantalum oxide layer on Pt(1 1 1), and the S/N of LEED and HREELS for the tantalum oxide layer was poor, compared with that for niobium oxide layer. However, it is suggested that the defect face of tantalum oxide is related to the activation of alkane. And the difference of the activation of alkane between the defect faces of tantalum oxide and niobium oxide is noted.

3. Selective oxidation of propane over mixed metal oxide catalysts

Niobium oxide and tantalum oxide easily react with many other metal oxides to form mixed metal oxide phases with complex structure. The ionic radius of Nb^{5+} is almost equal to that of Ta^{5+}. Similar physicochemical properties are expected for Nb containing mixed metal oxides and the corresponding Ta containing mixed metal oxides. Thorsteinson et al. [16] reported that Mo–V–Nb mixed metal oxide catalysts were effective for the oxidative dehydrogenation of ethane to ethene. We confirmed that Mo–V–Ta mixed metal oxide catalysts showed similar activities for the reaction.

Previously, we reported that Mo–V–Nb–Te mixed metal oxide catalysts were highly active and selective for the ammoxidation of propane to AN [4,5]. The different type of mixed metal oxides, V–Sb–O systems, are also the promising catalysts for the ammoxidation of propane [17]. The efficiency of the catalyst is higher than those of V–Sb–W and Bi–Mo catalysts under our standard reaction condition, as shown in Fig. 2. The high activity and selectivity of Mo–V–Nb–Te oxides were attributed to its ability to activate both propane and ammonia at low temperatures [6]. The temperature at which maximum propane conversion is reached by Mo–V–Nb–Te, V–Sb–W and Bi–Mo varies from 703 K for Mo–V–Nb–Te, via 773 K for V–Sb–W to 863 K for Bi–Mo (Fig. 2(a)). Maximum propane conversion is higher than 90% for all catalyst. While Mo–V–Nb–Te, V–Sb–W and Bi–Mo are able to convert propane when the temperature is raised high enough, the selectivity to AN is intrinsically higher for Mo–V–Nb–Te than for V–Sb–W and Bi–Mo (Fig. 2(b)). Since the specific surface area of Mo–V–Nb–Te ($8\,m^2\,g^{-1}$) is much more smaller than that of V–Sb–W ($90\,m^2\,g^{-1}$), the surface normalized rates of reaction of Mo–V–Nb–Te is greater than that of V–Sb–W (Fig. 2(c) and (d)). The AN selectivity of Mo–V–Nb–Te goes through a maximum of 61% at 693 K, while it increases with temperature for V–Sb–W to 32% at 803 K. AN selectivity of Bi–Mo shows a complicated dependence on the reaction temperature. Combination of the activity and selectivity data reveals that the yield of AN will be much higher for Mo–V–Nb–Te than for V–Sb–W and Bi–Mo. That is mainly due to the much higher selectivity for AN of Mo–V–Nb–Te.

However, Mo–V–Ta–Te was less active and selective for the ammoxidation of propane to AN than Mo–V–Nb–Te oxide catalysts, as shown in Table 3. For the preparation of Mo–V–Nb–Te, aqueous solution containing Nb, oxalate ion and substantially ammonium ion is usually used. We reported that hydrated niobium oxide dissolved warm aqueous oxalic acid solution [18]. The solubility of hydrated niobium oxide depends on the concentration of oxalic acid and temperature. However, more concentrated oxalic acid solution was necessary to dissolve hydrated tantalum oxide and to get the precursor of Mo–V–Ta–Te. Oxalic acid or oxalate ion acts as the reducing agent for the Mo–V–Nb(Ta)–Te oxide catalysts in the course of heat-treatment of the precursor. Hence, the oxidation state of the oxide catalysts was changed after the heat-treatment, and the catalytic performance was different. The crystal phases and surface chemical bonds of metal–oxygen are effective for the selective oxidation have been studied [5]. The effects of preparation method and conditions on the catalytic performance and the formation of crystal phases of these mixed metal oxides are discussed elsewhere.

Table 3
Catalytic activities of Mo–V–X–Y oxides for the ammoxidation of propane[a]

Catalyst	Reaction temperature (K)	Conversion of propane (%)	Selectivity for AN (%)
$Mo_1V_{0.4}Nb_{0.1}Te_{0.2}O_x$	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	0.0	–
$V_{0.4}Nb_{0.1}Te_{0.2}O_x$	703	0.6	–
$Mo_1V_{0.4}Ta_{0.1}Te_{0.2}O_x$	693	46.8	37.4

[a] Reaction conditions: catalyst amount = $0.5\,cm^3$, GHSV = $500\,h^{-1}$, C_3H_8/NH_3/air = 1/1.2/10 mol.

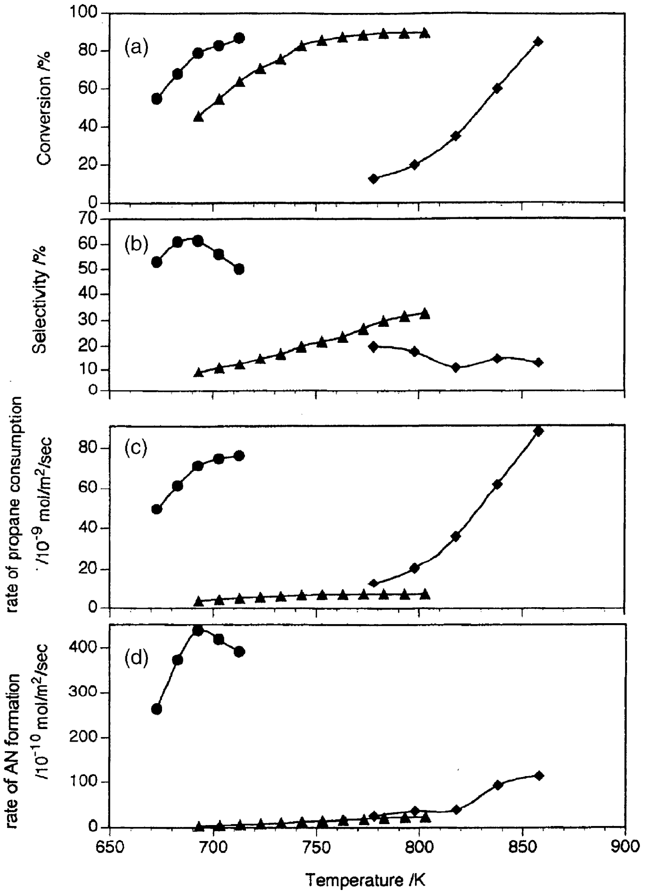


Fig. 2. (a) Conversion of propane, (b) selectivity for AN, (c) rate of propane consumption and (d) rate of AN formation of MoVNbTe catalyst (●), compared with VSbW (▲) and BiMo (◆) catalysts. Parts (c) and (d) are surface-normalized rates of reaction. Catalyst amount = 0.5 cm^3, GHSV = 1000 h^{-1}, C_3H_8/NH_3/air = 1/1.2/15 mol.

Table 4
Catalytic activities of Mo–V–Nb–Te oxide for the selective oxidation of propane to AA[a]

Reaction condition						Conversion of propane (%)	Selectivity for AA (%)	Yield of AA (%)
Temperature (K)	GHSV (h^{-1})	Concentration (mol%)						
		Propane	O_2	N_2	H_2O			
673	1734	6.3	18.8	75.0	–	75.3	42.4	31.9
653	1734	6.3	9.4	84.4	–	49.8	56.2	28.0
653	1854	6.3	18.8	75.0	–	63.3	48.4	30.6
663	1871	3.3	10.0	86.7	–	41.8	38.7	16.2
663	1871	3.3	10.0	40.0	46.7	65.7	58.0	38.1
693	1439	4.4	13.0	52.2	30.4	61.2	57.5	35.2
693	3247	1.9	5.8	23.1	69.2	69.0	52.5	36.2
653	1861	3.3	10.0	40.0	46.7	80.1	60.5	48.5

[a] Catalyst: $Mo_1V_{0.3}Nb_{0.12}Te_{0.23}O_x$.

Mo–V–Nb–Te oxide catalysts exhibit high efficiency for AA production from propane without ammonia, as shown in Table 4. The addition of steam to the reactant mixture was effective for the increase of selectivity for AA, especially at the higher propane conversion [7].

The active components of Mo–V–Nb–Te oxide catalysts have been shown to be two crystal phases called M1 and M2 [5]. And the structure and synthesis of these crystal phases have been investigated. The results will be reported elsewhere.

4. Conclusion

Niobium and tantalum are important elements for the activation of alkanes in the viewpoints of acidic property and the formation of unique mixed metal oxides. And the difference of the ability of alkane activation between niobium- and tantalum-based oxide catalysts is studied. The following key points emerge from this study:

(1) Niobium oxide and tantalum oxide show strong acid property and seem to promote the activation of alkanes. Hydrated tantalum oxide is activated to a solid superacid by the treatment with sulfuric acid. The sulfuric acid treated hydrated tantalum oxide (H_2SO_4/TA) isomerizes *n*-butane to isobutane at room temperature.
(2) H_2SO_4/TA activates P–Mo–V heteropolyacid compounds for the selective oxidation of isobutane to MAL and MAA. The combination of the strong acid component (H_2SO_4/TA) and the selective oxidation component (P–Mo–V heteropolyacid compounds) for the olefinic compounds is effective for the reaction.
(3) However, hydrated niobium oxide is not activated to a solid superacid by the treatment with sulfuric acid.
(4) The difference of adsorption phenomena of *n*-butane on the defect face of surface metal oxide layer between niobium and tantalum is related to the difference of ability of alkane activation.
(5) Mo–V–Nb–Te mixed metal oxide catalysts are active for the ammoxidation of propane to AN. However, Mo–V–Ta–Te mixed metal oxide is less active. The preparation of catalysts, especially the concentration of oxalic acid in the aqueous solutions containing Nb or Ta, that is, the raw material of mixed metal oxides seem to affect the condition of the catalyst.
(6) Mo–V–Nb–Te mixed metal oxide catalysts are also active for the oxidation of propane to AA.

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