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Acidic and Catalytic Properties of Niobium Pentaoxide

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The surface acidic property of $Nb_2O_5 \cdot nH_2O$ and its catalytic activities for the isomerization of 1-butene, the polymerization of propylene and the dehydration of 2-butanol were examined. The activities were high on $Nb_2O_5 \cdot nH_2O$ evacuated at moderate temperatures (100—150 °C) in all of the reactions and decreased drastically on evacuation at higher temperatures (400—500 °C). The surface of $Nb_2O_5 \cdot nH_2O$ showed a strong acidic character ($H_0 \leq -5.6$) even after heating in air at 100 °C, but the strong acid sites disappeared on heat treatment at higher temperatures. The active sites on the catalysts heat-treated at moderate temperatures were ascribed mainly to Brönsted acid sites on the basis of the IR study of adsorbed pyridine.

Although niobium oxides are reported in the patents to catalyze several reactions such as the oxidation of organic molecules,[1] oxidative dehydrogenation of olefins or paraffins,[2] and the decomposition of NO_x,[3] the details of surface property and catalytic activity are not known. On the other hand, catalysts containing molybdenum and vanadium, neighbors of niobium in the periodic table, are the most important industrial catalysts and their catalytic properties have been studied extensively by many workers. In this sense, it will be possible to use niobium oxides as a catalyst or an active component of catalysts for certain reaction. For this purpose, a fundamental knowledge about niobium oxides is required. Thus, we have studied the surface acid-base properties and the catalytic activities for the reactions of 1-butene, propylene, and 2-butanol as model reactions.

Experimental

Niobium oxide was prepared by heating $Nb_2O_5 \cdot nH_2O$ (CBMM AD-108) in a vacuum or in air at various temperatures. The $Nb_2O_5 \cdot nH_2O$ was used after washing with distilled water followed by drying at 100 °C. The content of Nb in $Nb_2O_5 \cdot nH_2O$ was 55.54% and no impurity of K or Na was detected.

The differential thermal analysis (DTA) and thermogravimetry (TG) were done by using a Rigaku TG-DTA apparatus with the heating program rate of 10 °C/min. The X-ray diffraction pattern was taken by a Shimadzu XRD spectrometer with Cu *Ka* source. The surface area of $Nb_2O_5 \cdot nH_2O$ was measured by using a conventional BET apparatus.

For the measurement of acidic and basic properties, Nb_2O_5 was suspended in a benzene solution, basic or acidic indicators were adsorbed and the color change of indicators was observed.[4] The indicators used were anthraquinone ($pK_a = -8.2$), benzylideneacetophenone (−5.6), dicinnamylideneacetone (−3.0), Crystal Violet (+0.8), 4-anilinoazobenzene (+1.5), 4-dimethylaminoazobenzene (+3.3), Methyl Red (+4.8), and Bromthymol Blue (+7.1).

Infrared spectra were recorded with a JASCO-701G spectrometer using an in situ cell. The sample was pressed into a thin wafer and placed in the cell. Pyridine was adsorbed on $Nb_2O_5 \cdot nH_2O$ which had been evacuated at various temperatures for 2 h and degassed at certain temperatures for 30 min. The IR spectra of adsorbed CO_2 was also measured by the same method as in pyridine adsorption.

For the reactions of 1-butene and 2-butanol, a closed recirculation reactor having a volume of 300 cm^3 was used. After the evacuation of $Nb_2O_5 \cdot nH_2O$ at various temperatures for 2 h, 6.7 kPa of 1-butene or 1.4 kPa of 2-butanol was introduced at the reaction temperature. The polymerization activity of propylene was measured by observing the pressure decrease in a static reactor. The activity was obtained by measuring the rate of decrease in reactant pressure (initial pressure = 13.3 kPa) at 5 min reaction time to avoid the pressure decrease due to the adsorption in the initial stage of the reaction.

Results

X-Ray and Thermal Analysis of $Nb_2O_5 \cdot nH_2O$. The results of DTA and TG of $Nb_2O_5 \cdot nH_2O$ are shown in Fig. 1(A). At around 90 and 180 °C, two endothermic peaks with the decrease of gravity were observed. These can be ascribed to the dehydration process of $Nb_2O_5 \cdot nH_2O$. The dehydration was completed by heating up to 300 °C and the gravity change of the sample was not observed at 300—700 °C. The exothermic peak at

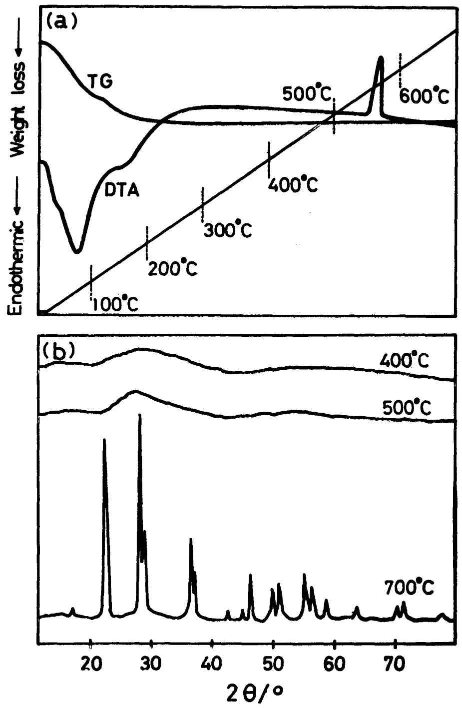

Fig. 1. (A) Thermogravimetry and differential thermal analysis of $Nb_2O_5 \cdot nH_2O$. (B) X-Ray diffraction patterns of $Nb_2O_5 \cdot nH_2O$ heat-treated at various temperatures in air.

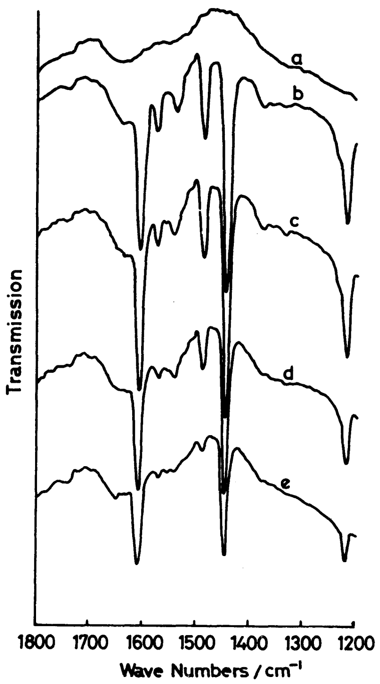

Fig. 2. IR spectra of pyridine adsorbed on $Nb_2O_5 \cdot nH_2O$. a: Background, b: degassed at room temperature after the adsorption, c: degassed at 100 °C, d: degassed at 200 °C, e: degassed at 300 °C.

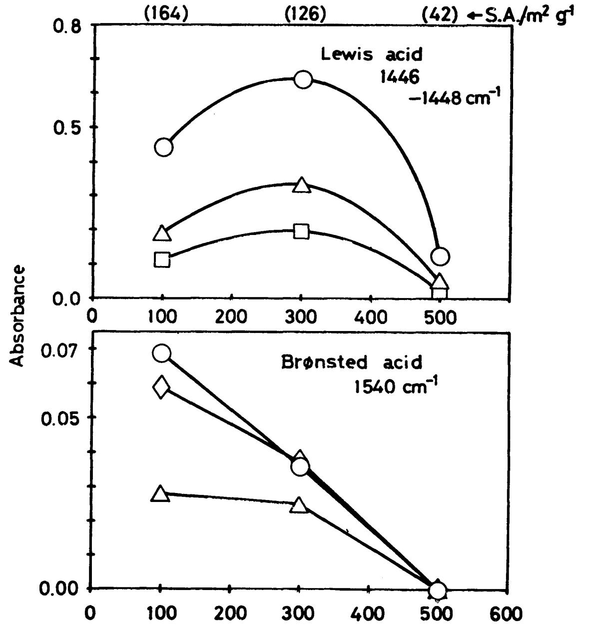

Fig. 3. Acidity change of $Nb_2O_5 \cdot nH_2O$ with pretreatment temperature.
◇: Evacuated at room temperature after adsorption of pyridine, ○: at 100 °C, △: at 200 °C, □: at 300 °C.

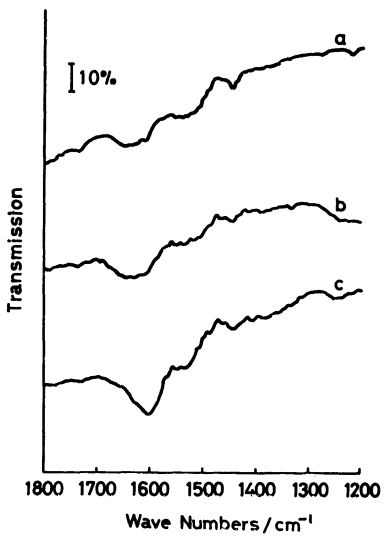

Fig. 4. IR spectra of CO_2 adsorbed on $Nb_2O_5 \cdot nH_2O$ evacuated at 300 °C, a: background, b: evacucated at room temperature after the adsorption for 15 min, c: adsorption for 15 h.

about 550—570 °C with no gravity change might be due to a phase transformation.

X-Ray diffraction patterns of the samples which were heat-treated at different temperatures are shown in Fig. 1(B). After heating $Nb_2O_5 \cdot nH_2O$ at 400 °C in air, very broad peaks at $2\theta \simeq 30°$ and around 55° were observed. Upon heating at 500 °C in air, those peaks sharpened slightly. A good crystallinity was observed by heating at 700 °C and the diffraction pattern corresponded well to the T–T phase Nb_2O_5.[5]

The surface areas of $Nb_2O_5 \cdot nH_2O$ were 164, 126, and 42 $m^2 g^{-1}$ after the evacuation at 100, 300, and 500 °C, respectively.

Acidic and Basic Character of $Nb_2O_5 \cdot nH_2O$. The acid strength of $Nb_2O_5 \cdot nH_2O$ examined by the indicator adsorption method is mentioned first. After drying at 100 °C, $Nb_2O_5 \cdot nH_2O$ changed the color of benzylideneacetophenone ($pK_a = -5.6$) indicator to its acidic color (yellow), but no color change of anthraquinone ($pK_a = -8.2$) was observed. After heat treatment at 300 °C, all the indicators of $pK_a \geqq -8.2$ also changed their colors to those of the acidic forms. Thus, $Nb_2O_5 \cdot nH_2O$ which was heated at 100—300 °C has an acid strength of $H_0 \leqq -5.6$. However, the strong acid sites disappeared and only an acid strength of $H_0 \leqq +3.3$ was observed by heating at 500 °C.

In order to obtain further information about the acidity of $Nb_2O_5 \cdot nH_2O$, the infrared spectroscopic study of the adsorbed pyridine was examined. The results are shown in Fig. 2. Upon the adsorption of pyridine over $Nb_2O_5 \cdot nH_2O$ which had been evacuated at various temperatures, the bands at 1610, 1540, 1480, and 1440 cm^{-1} were observed after degassing at 100—150 °C. The bands at 1610, 1480, and 1440 cm^{-1} are due to coordinated pyridine and the band at 1540 cm^{-1} is ascribed to pyridinium ion.[6] Thus, $Nb_2O_5 \cdot nH_2O$ has both Lewis and Brönsted acid sites on the surface. The pyridinium ion band almost disappeared after degassing at 300 °C, but the Lewis acid bands still remained. The band intensity changes with evacuation temperature on $Nb_2O_5 \cdot nH_2O$ which had been preheated in a vacuum at different temperatures are shown in Fig. 3. The Brönsted acid band intensity was strongest on the sample evacuated at 100 °C and decreased with the increase of

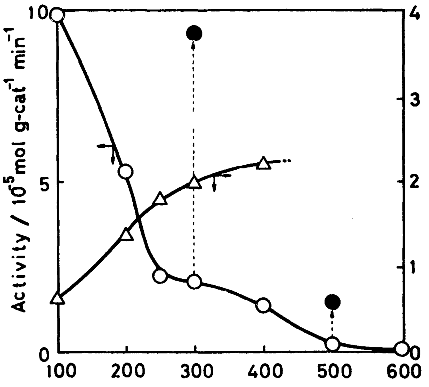

Fig. 5. Activity and selectivity of 1-butene isomerization. ●: H_2O added after pretreatment and evacuated at 100 °C.

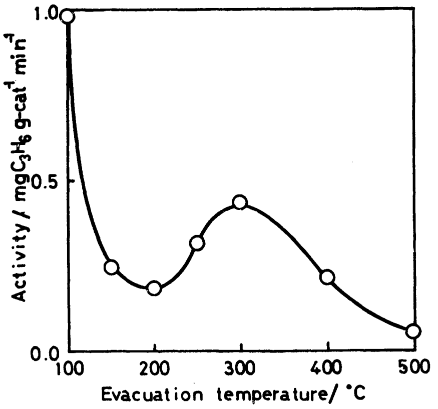

Fig. 6. Polymerization activity of propylene over $Nb_2O_5 \cdot nH_2O$.

pretreatment temperature. However, Lewis acid band intensity showed a maximum on the sample which had been evacuated at 300 °C. Upon preheating at 500 °C, both the acidic sites decreased remarkably.

The adsorption of CO_2 on $Nb_2O_5 \cdot nH_2O$ was examined to obtain an information about surface basic property. The spectra are shown in Fig. 4. After the introduction of CO_2 (2.7 kPa) on the sample which had been evacuated at 300 °C, no distinct change on the spectrum was observed. When the sample was contacted with CO_2 for 15 h, a slight increase of the bands at 1600 and 1390 cm^{-1} were noticed.

Isomerization of 1-Butene. The activity and selectivity changes of 1-butene isomerization with evacuation temperature are shown in Fig. 5. The $Nb_2O_5 \cdot nH_2O$ which was evacuated at 100 °C for 2 h showed a remarkable isomerization activity, the selectivity (the ratio of *cis*-2-butene to *trans*-2-butene) being less than unity. However, if the pretreatment temperature was increased to 200—250 °C, the activity decreased remarkably and the selectivity increased to about 2. In the range of evacuation temperature of 250—400 °C, the activity was not sensitive to the treatment temperature but diminished after the treatment at 500—600 °C. When $Nb_2O_5 \cdot nH_2O$ which had been evacuated at 300 °C was exposed to H_2O vapor at room temperature followed by evacuation at 100 °C, almost the same activity as the catalyst originally evacuated at 100 °C was restored. On the other hand, after evacuation at 500 °C, the activity actually increased by the same treatment but the effect was far less compared to the case evacuated at 300 °C.

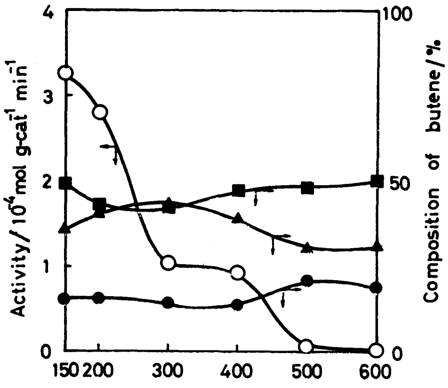

Fig. 7. Activity and selectivity changes of 2-butanol over $Nb_2O_5 \cdot nH_2O$ evacuated at various temperatures. ●: 1-Butene, ▲: *trans*-2-butene, ■: *cis*-2-butene

Polymerization of Propylene. The change of polymerization activity at 100 °C with evacuation temperature is shown in Fig. 6. The activity was highest on the sample evacuated at 100 °C and decreased remarkably after evacuation at 150—200 °C. However, upon evacuation at higher temperatures, the activity increased again and attained a maximum on treatment at 300 °C. After evacuation at the temperatures higher than 500 °C, the catalyst became almost inactive. The products of polymerization were not thoroughly analyzed due to the adsorption on the sample, but a considerable amount of butenes and pentenes along with the higher hydrocarbons desorbed at higher temperature (300 °C).

Dehydration of 2-Butanol. The changes of activity and selectivity of 2-butanol dehydration reaction with evacuation temperature are shown in Fig. 7. The activity gradually decreased with evacuation temperature. However, the activity was not changed by evacuation between 300—400 °C. The activity finally diminished on evacuation at 500—600 °C.

The formation of dehydrogenated product was not observed in the reaction at 150 °C over the whole catalysts. The ratio of formed *cis*- and *trans*-2-butenes was almost unity and the amount of 1-butene was less than 20% of the products over the catalysts evacuated at lower temperatures (150—300 °C), but the amount of 1-butene increased and that of *trans*-2-butene decreased after evacuation at 400—500 °C.

Discussion

The surface of $Nb_2O_5 \cdot nH_2O$ showed a considerable strong acidic character and rather weak basic property. After heat treatment at 100 °C, the strong acid sites of $H_0 \leq -5.6$ were found to exist on the surface. Over the typical solid acid catalysts such as SiO_2–Al_2O_3 and SiO_2–TiO_2, the strong acid sites appear only after heat treatment at high temperature ($\simeq$500 °C)$^{7)}$ along with the removal of surface water. The acid sites on those catalyst surfaces are thought to be the isolated OH groups as Brönsted acid sites and the exposed metal ions as Lewis acid sites both of which appear after rigorous heat treatment.[7] However, $Nb_2O_5 \cdot nH_2O$ has acidic OH groups (Brönsted acid sites) as observed by IR experiment even after the mild heat treatment at 100 °C. Thus, the surface acidic property of $Nb_2O_5 \cdot nH_2O$ pretreated at mild temperatures is very peculiar and interesting because the residual water might cover almost the whole surface after the treatment. Upon pretreatment at 300 °C, H_2O was almost removed from $Nb_2O_5 \cdot nH_2O$ as observed in DTA experiment, and Lewis acidity increased along with the decrease of Brönsted acidity. However, after treatment at 500 °C, Nb_2O_5 became very inactive and the acidic property was very weak. This surface change is considered to be due to a phase transformation of amorphous $Nb_2O_5 \cdot nH_2O$ to T–T phase Nb_2O_5[5] at around 500—600 °C as observed by DTA and XRD. The catalytic activity of Nb_2O_5 was diminished by heat treatment at 500 °C or higher temperatures in the whole cases of 1-butene isomerization, propylene polymerization and 2-butanol dehydration reactions. In the case of 1-butene isomerization, $Nb_2O_5 \cdot nH_2O$ was very active on evacuation at 100 °C. The ratio of produced cis- and trans-isomers was around unity as observed in a typical case of acid-catalyzed reaction over SiO_2–Al_2O_3.[8] Though the activity decreased drastically after the sample was evacuated at 300 °C, almost the same activity as the sample evacuated at 100 °C was restored only by the introduction of H_2O vapor followed by evacuation at 100 °C. This fact indicates that the isomerization is catalyzed mainly by Brönsted acid sites whose amount decreases with the increase of evacuation temperature as shown in Fig. 3. However, after evacuation at 500 °C, only a slight increase of activity was observed by the introduction of H_2O vapor. The decrease of surface area due to the phase transformation at around 500 °C might prevent the regeneration of Brönsted acid sites on the surface.

In the reaction of 2-butanol dehydration, a high activity was achieved by evacuation at 150—200 °C. The activity on the catalyst evacuated at 150 °C was almost comparable to that on SiO_2–Al_2O_3 (3.7×10^{-4} mol min^{-1} g^{-1} at 200 °C).[9] Since the activity was reduced remarkably by evacuation at 300 °C, the activity would be also ascribed to Brönsted acidity, but Lewis acid sites might also act as active sites on evacuation at 300—400 °C. It is known that the selectivity of produced butenes from 2-butanol is very sensitive to the surface acidic and basic property.[10] The oxide catalysts which have both acidic and basic sites such as ThO_2 and ZrO_2 produce 1-butene dominantly.[11] However, over the strongly acidic catalysts such as SiO_2–Al_2O_3 produce less amount of 1-butene than 2-butene.[12] The $Nb_2O_5 \cdot nH_2O$ in this experiment is the latter case. It would be reasonable because the surface of $Nb_2O_5 \cdot nH_2O$ was mainly acidic and only very weak basic sites were observed in IR of CO_2 adsorption or indicator adsorption.

The polymerization of propylene is known as a model reaction catalyzed by Brönsted acid sites over SiO_2–Al_2O_3 or other acid catalysts.[13] In this work, $Nb_2O_5 \cdot nH_2O$ evacuated at 100 °C showed the highest activity for the polymerization, but the activity decreased remarkably when evacuated at 200—250 °C. In this case, it might be reasonable that the activity is ascribed to Brönsted acidity. However, the activity increased again on evacuation at 300—400 °C in contrast to the cases of 1-butene isomerization and dehydration of 2-butanol. This fact suggests the importance of Lewis acidity in the polymerization of propylene over Nb_2O_5 evacuated at higher temperatures. It is known that niobium compounds such as niobium trichloride distearate and niobium tetrachloride butanoate can polymerize ethylene, propylene, and 1,3-butadiene.[14] The promoting effect of niobium halide in the polymerization in Ziegler-Natta system is also known in the patent.[15] Since the importance of niobium ion as an active site for the polymerization is apparent in those cases, the Lewis acid site is thought to be an active site even on the oxide of niobium. Thus, we conclude that the polymerization of propylene proceeds on Brönsted acid sites on $Nb_2O_5 \cdot nH_2O$ pretreated at low temperatures ($\simeq$100 °C), but Lewis acid sites become main active sites after treatment at higher temperatures.

In conclusion, niobium oxide treated at 100 °C is characterized as a very strong Brönsted acid and can be used as a potential catalyst for Brönsted acid-catalyzed reactions at mild conditions. It should be emphasized that niobium oxide exhibits the highest acid strength among all of the metal oxides pretreated at 100 °C.

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