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SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



No. 08-079287- -00004-0000

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Referencia	Expediente No. 08-079287
Asunto	Solicitud de patente para: PROCEDIMIENTO PARA LA PRODUCCIÓN DE BIODIESEL A PARTIR DE ACEITES VEGETALES Y GRASAS UTILIZANDO CATALIZADORES HETEROGENEOS
Solicitante	PETROLEO BRASILEIRO S.A. - PETROBRAS
Fecha de solicitud	3 de julio de 2008

1. Yo, Luz Clemencia DE PÁEZ, en mi condición de apoderada de la sociedad solicitante de la patente de la referencia, me refiero al oficio No. **11027** notificado por fijación en lista del 22 de junio de 2012.
2. Mediante oficio No. **11027** el Examinador a cargo del estudio de patentabilidad de la presente solicitud, en virtud del artículo 46 de la Decisión 486, solicitó la presentación de los siguientes documentos:
 - 2.1 S. Okazaki and A. Kurosaki: "Acidic properties and catalytic activities of niobic acid treated with phosphoric acid". Catalyst Today; volume 8, Issue 1.
 - 2.2 Jih-Mim Jehng and Israel E. Wachs: "Niobium oxalate new precursor for preparation of supported niobium oxide catalyst". American Chemical Society. Volume 437, chapter 21, September 21st, 1990, p. 232-242.

3. Respuesta al requerimiento

Con el ánimo de dar respuesta al requerimiento formulado por el Examinador, se presenta junto con el presente memorial, copia de los dos documentos arriba mencionados.

4. Puesto que se han atendido a cabalidad las observaciones hechas por su Despacho sobre la presente solicitud de patente, atentamente solicito que se continúe su tramitación.

5. Anexos

- 5.1 S. Okazaki and A. Kurosaki: "Acidic properties and catalytic activities of niobic acid treated with phosphoric acid". Catalyst Today; volume 8, Issue 1.
- 5.2 Jih-Mim Jehng and Israel E. Wachs: "Niobium oxalate new precursor for preparation of supported niobium oxide catalyst". American Chemical Society. Volume 437, chapter 21, September 21st, 1990, p. 232-242.

Señor Director,


LUZ CLEMENCIA DE PÁEZ

C.C. 35.456.344 de Usaquén

T.P.A. No. 23.555

Chapter 21

Niobium Oxalate

New Precursor for Preparation of Supported Niobium Oxide Catalysts

Jih-Mirn Jehng and Israel E. Wachs

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The aqueous preparation of supported niobium oxide catalysts was developed by using niobium oxalate as a precursor. The molecular states of aqueous niobium oxalate solutions were investigated by Raman spectroscopy as a function of pH. The results show that two kinds of niobium ionic species exist in solution and their relative concentrations depend on the solution pH and the oxalic acid concentration. The supported niobium oxide catalysts were prepared by the incipient wetness impregnation technique and characterized by Raman, XRD, XPS, and FTIR as a function of niobium oxide coverage and calcination temperature. The Raman studies reveal that two types of surface niobium oxide species exist on the alumina support and their relative concentrations depend on niobium oxide coverage. Raman, XRD, XPS, and FTIR results indicate that a monolayer of surface niobium oxide corresponds to ~ 19% Nb_2O_5 for an Al_2O_3 support possessing ~ 180 m^2/g . The surface niobium oxide phase is found to be stable to high calcination temperatures.

Supported niobium oxide catalysts have recently been shown to be effective catalysts for many catalytic reactions: pollution abatement, selective oxidation, hydrocarbon conversion, carbon monoxide hydrogenation, etc. [1]. In a previous study [2], it was shown that the presence of the surface niobium oxide phases retards the loss in surface area of the Al_2O_3 and TiO_2 supports and stabilizes the $\text{V}_2\text{O}_5/\text{TiO}_2$ system during high temperature treatments. The surface niobium oxide species on the Al_2O_3 support was also found to possess

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In Novel Materials in Heterogeneous Catalysis; Baker, R., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1990.

strong Bronsted acidity [3]. These important properties impart the surface niobium oxide phase on the Al_2O_3 support with a high hydrocarbon cracking activity at elevated temperatures.

Niobium ethoxide $[\text{Nb}(\text{OC}_2\text{H}_5)_5]$ has traditionally been used as a precursor for the preparation of supported niobium oxide catalysts. This non-aqueous preparation method requires a controlled environment and special procedures to avoid the decomposition of the niobium ethoxide in the presence of moisture. It is well-known that transition metal ions form a stable solution chelate with oxalate groups, and molybdenum oxalate [4] and vanadium oxalate [5] have been widely used for the aqueous preparation of supported molybdenum oxide and supported vanadium oxide catalysts. In the present study, niobium oxalate $[\text{Nb}(\text{HC}_2\text{O}_4)_5]$ was investigated as an aqueous precursor for the preparation of supported niobium oxide catalysts.

EXPERIMENTAL METHODS

Materials and Preparation Methods

Niobium oxalate was supplied by Niobium Products Company with the following chemical analysis: 20.5% Nb_2O_5 , 790 ppm Fe, 680 ppm Si, and 0.1% insolubles. Niobium oxalate was dissolved into a constant concentration of aqueous oxalic acid solution, and the pH of the solution was varied from 0.50 to 5.00 by adding ammonium hydroxide. The supported niobium oxide on Al_2O_3 catalysts were prepared by the incipient-wetness impregnation method using the niobium oxalate/oxalic acid aqueous solution and Al_2O_3 (Harshaw, 180 m^2/g). The samples were dried at 110–120°C for 16 hours, and then calcined at 500°C under flowing dry air for 16 hours.

Raman Spectroscopy

Raman spectra were obtained with a Spex Triplemate spectrometer (Model 1877) coupled to an EG&G intensified photodiode array detector cooled thermoelectrically to -40°C, and interfaced with an EG&G OMA III Optical Multichannel Analyzer (Model 1463). The samples were excited with the 514.5 nm Ar^+ laser. The beam was focused on the sample illuminator where the sample typically spins at about 2000 rpm to avoid local heating. The Raman scattering was collected by the spectrometer, and analyzed with an OMA III built-in software package. The overall spectral resolution of the spectra is about 2 cm^{-1} .

X-Ray Powder Diffraction (XRD)

The crystalline Nb_2O_5 phase in the supported niobium oxide catalysts was detected by an APD 3600 automated X-

ray powdered diffractometer using Cu K_α (45KV, 30MA) radiation. The $\text{Nb}_2\text{O}_5/\text{Al}_2\text{O}_3$ samples were calcined at 700°C to increase the Nb_2O_5 particle size and enhance the XRD signals.

X-Ray Photoelectron Spectroscopy (XPS)

XPS experiments were performed on a Physical Electronic Instruments ESCA/AUGER system. The samples were placed on the sample holder at a 45° angle to the entrance of analyzer and the system was evacuated to 10^{-9} - 10^{-10} Torr. The XPS spectra were calibrated against the Au $4f_{7/2}$ peak using the Mg K_α line as the X-ray exciting radiation.

CO_2 Chemisorption

The CO_2 uptake of supported niobium oxide on Al_2O_3 at different Nb_2O_5 loadings was measured with a Quantasorb BET apparatus using a 1:9 ratio of CO_2/He mixture gases. The samples were degassed at 250°C for 2 hours under flowing He, and the CO_2 chemisorption was performed at room temperature.

RESULTS AND DISCUSSION

Niobium oxide reference compounds

The Raman spectra of several niobium oxide compounds, with their corresponding symmetry and coordination, are shown in Figure 1. The $\text{Nb}_6\text{O}_{19}^{8-}$ unit is a well-characterized structure which consists of three different types of Nb-O bonds at each niobium center: a short Nb=O terminal double bond, a longer Nb-O-Nb bridging bond, and a very long and weak Nb---O single bond connected to the center of the cage-like octahedral structure [6-8]. From the known structure of $\text{K}_8\text{Nb}_6\text{O}_{19}$ the main frequencies of the $\text{K}_8\text{Nb}_6\text{O}_{19}$ Raman spectrum in Figure 1 can be assigned: Nb=O terminal stretching mode (903, 879, and 831 cm^{-1}), corner or edge-shared octahedral NbO_6 stretching mode (734, 537, and 463 cm^{-1}), Nb=O bending mode (289 cm^{-1}), and Nb-O-Nb bending mode (223 cm^{-1}). The multiple terminal stretching modes present in the high wavenumber region are due to distortions present in the $\text{K}_8\text{Nb}_6\text{O}_{19}$ structure. Niobium pentoxide, Nb_2O_5 , possesses a more order octahedral structure with no Nb=O terminal bonds, and a major band appears at 690 cm^{-1} which is characteristic of an octahedral NbO_6 stretching mode as well as Nb-O and Nb-O-Nb bending modes at $\sim 300\text{ cm}^{-1}$ and $\sim 230\text{ cm}^{-1}$, respectively. For the niobium oxalate precursor a sharp and strong Raman band is present at 958 cm^{-1} due to a Nb=O terminal bond and the associated bending modes appear in the $200\text{--}400\text{ cm}^{-1}$ region. The Raman band at

$\sim 570\text{ cm}^{-1}$ arises from the bidentate oxalate ligands coordinated to the niobium [9,10]. The Raman frequencies of the reference compounds are tabulated in Table 1.

Niobium Oxalate Aqueous Solutions

Niobium oxalate has a low solubility in aqueous solutions, but its solubility can be dramatically increased by the addition of oxalic acid to the aqueous solutions. At high oxalic acid concentrations, however, the niobium oxalate and oxalic acid precipitate from solution. The solubility curve of niobium oxalate in aqueous solutions is shown in Figure 2 as a function of the oxalic acid concentrations. Figure 3 shows a series of Raman spectra of the niobium oxalate in aqueous oxalic acid solutions with varying pH (0.50 to 5.00). At low pH (<3.00), two peaks are observed in the $900\text{--}1000\text{ cm}^{-1}$ region which are characteristic of Nb=O terminal stretching modes. The behavior of these two peaks with pH variation suggests that two niobium oxalate species exist in solution. The associated bending modes appear in $200\text{--}400\text{ cm}^{-1}$ region. A Nb-O₂-C₂ breathing mode also appears at $\sim 570\text{ cm}^{-1}$. At high pH (>5.00), two new Raman bands form at $\sim 670\text{ cm}^{-1}$ and $\sim 220\text{ cm}^{-1}$ which indicate the formation of hydrated Nb₂O₅.

It is known that the niobium oxide complexes in oxalic acid aqueous solutions display an equilibria between two ionic species containing 2 or 3 oxalate groups which depend on the solution pH and the oxalic acid concentration [11,12]. Thus, the two Nb=O terminal bonds appearing in the aqueous Raman spectra are assigned to the two different niobium oxalate ionic species present in the solution. The Raman spectra also show that the relative intensity of two Nb=O bands, $\sim 910\text{ cm}^{-1}$ and $\sim 930\text{ cm}^{-1}$, changes with increasing pH. When ammonium hydroxide is added to the solution, the niobium oxalate species with 3 oxalate groups starts to hydrolyze to 2 oxalate groups as one of the oxalate groups is replaced by OH groups. This results in an increase in intensity of the $\sim 910\text{ cm}^{-1}$ Nb=O band with increasing solution pH. Increasing the pH to about 5.00 by further addition of ammonium hydroxide causes the niobium oxalate species to hydrolyze and coagulate to a hydrated Nb₂O₅ precipitate. The aqueous solution chemistry of niobium oxalate is shown below:

Table 1: Raman frequencies of bulk niobium oxide compounds

Vibrational Modes	Wavenumber (cm ⁻¹)		
	K ₈ Nb ₆ O ₁₉	Nb ₂ O ₅	Nb(HC ₂ O ₄) ₅
ν(Nb=O)	903,879,831	-	958
ν(NbO ₆)	734 537 463	690	-
ν(NbO ₂ C ₂)	-	-	572
δ(Nb-O)	289	302	284
δ(Nb-O-Nb)	223	238	243

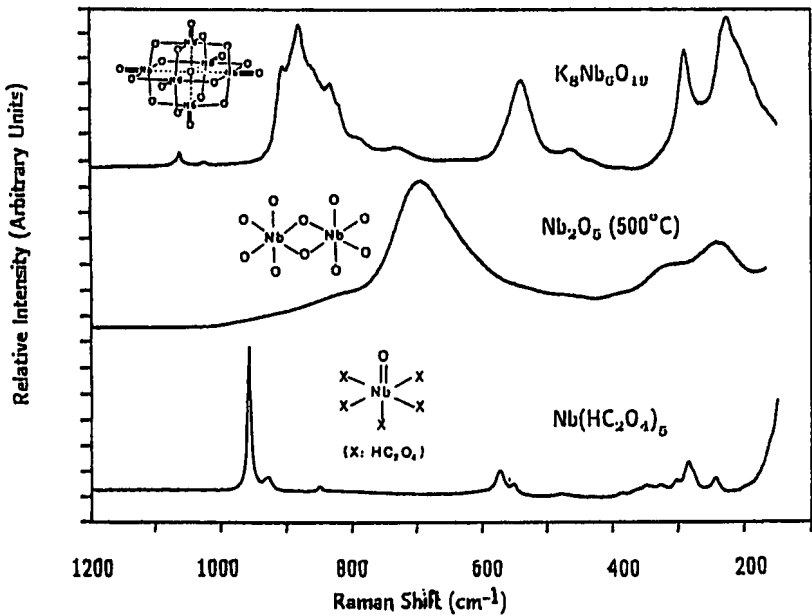


Figure 1: The solubility of nioibum oxalate in solution as a function of oxalic acid added.

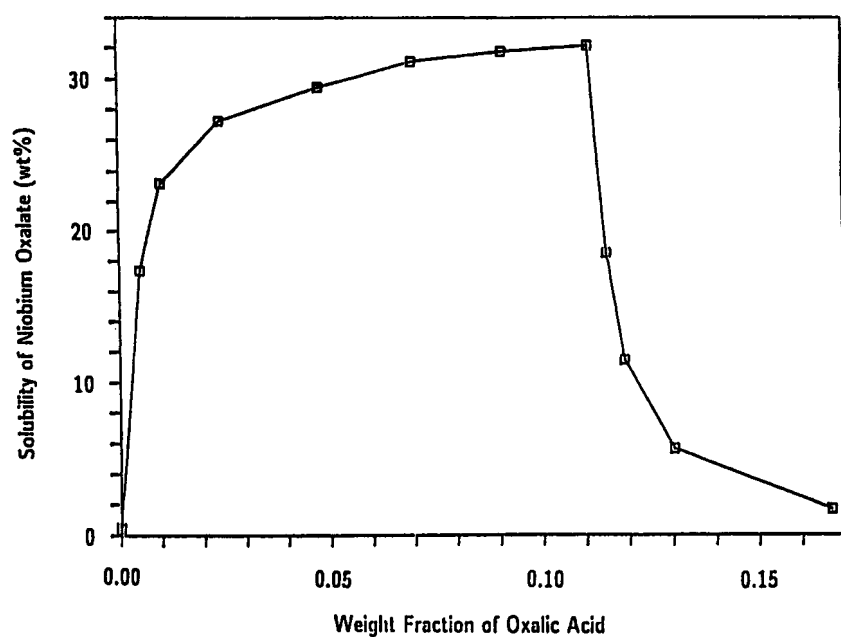


Figure 2: Raman spectra of bulk niobium oxide compounds.

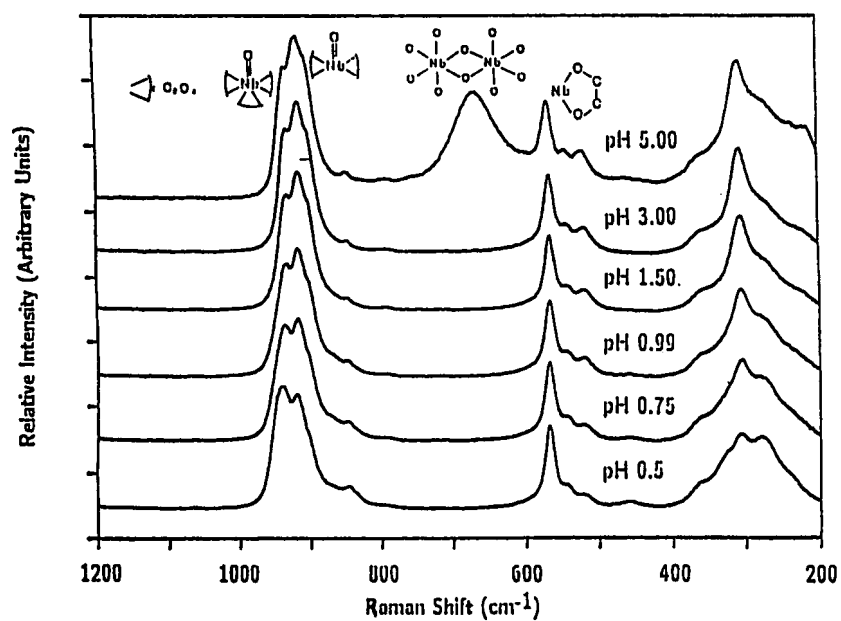
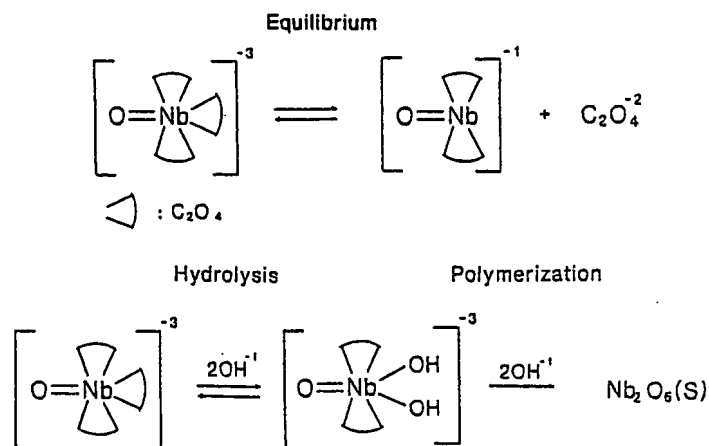


Figure 3: Raman spectra of niobium oxalate in oxalic acid solution as a function of pH from 0.5 to 5.00.



Supported Niobium Oxide on Alumina

The Raman spectra of supported niobium oxide on alumina are shown in Figure 4 as a function of Nb_2O_5 loading. The nature of the supported niobium oxide phase is determined by comparison of the Raman spectra of the supported niobium oxide samples with those of niobium oxide reference compounds. The Raman features of 1-22% $\text{Nb}_2\text{O}_5/\text{Al}_2\text{O}_3$ samples are different than the bulk niobium oxide compounds due to the formation of a two-dimensional surface niobium oxide overlayer on the alumina support [2]. At low surface coverages (<8% $\text{Nb}_2\text{O}_5/\text{Al}_2\text{O}_3$), the weak and broad Raman band in the 890-910 cm^{-1} region is present due to a distorted octahedral (approaching square-pyramidal) surface niobium oxide species possessing $\text{Nb}=\text{O}$ bonds, and the mode at $\sim 230 \text{ cm}^{-1}$ is characteristic of a $\text{Nb}-\text{O}-\text{Nb}$ linkage. At high surface coverages (>8% $\text{Nb}_2\text{O}_5/\text{Al}_2\text{O}_3$), an additional Raman band at $\sim 630 \text{ cm}^{-1}$ is also present due to a slightly distorted octahedral surface niobium oxide species. The Raman studies reveal that two types of surface niobium oxide species exist on the alumina support, and that their relative concentrations depend on the surface niobium oxide coverage.

A series of supported niobium oxide on alumina catalysts, 0-45% $\text{Nb}_2\text{O}_5/\text{Al}_2\text{O}_3$, were further characterized by XRD, XPS, CO_2 chemisorption, as well as Raman spectroscopy in order to determine the monolayer content of the $\text{Nb}_2\text{O}_5/\text{Al}_2\text{O}_3$ system. The transition from a two-dimensional metal oxide overlayer to three-dimensional metal oxide particles can be detected by monitoring the

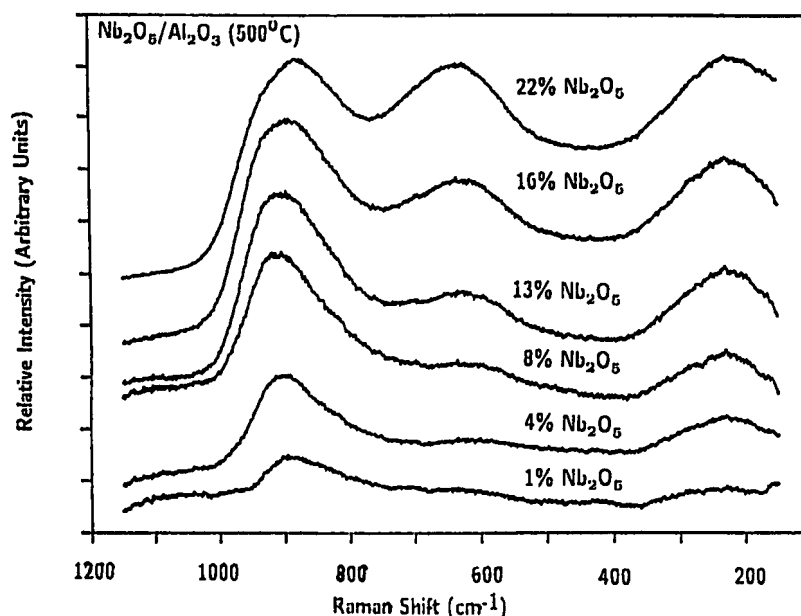


Figure 4: Raman spectra of $\text{Nb}_2\text{O}_5/\text{Al}_2\text{O}_3$ (500°C) as a function of niobium oxide coverage.

(Nb/Al)_{surface} ratios in such systems with XPS because of the vastly different XPS cross-sections of these two phases [13]. The (Nb/Al)_{surface} ratios of the niobium oxide on the alumina support were obtained by integrating the areas of the Nb 3d_{3/2,5/2} and the Al 2p photoelectron lines, and the (Nb/Al)_{surface} vs. (Nb/Al)_{bulk} curve is shown in Figure 5. The break in the curve corresponds to ~19% $\text{Nb}_2\text{O}_5/\text{Al}_2\text{O}_3$ and suggests that the transition from a two-dimensional phase to three-dimensional particles, monolayer coverage, occurs at this point. This conclusion is supported by XRD measurements which only detect crystalline Nb_2O_5 particles above 19% $\text{Nb}_2\text{O}_5/\text{Al}_2\text{O}_3$, and CO_2 chemisorption measurements (see Figure 6) which indicate that the basic alumina hydroxyls have been removed by the niobium oxide overlayer [14,15]. The slight increase in the CO_2 chemisorption above 19% $\text{Nb}_2\text{O}_5/\text{Al}_2\text{O}_3$ is due to CO_2 chemisorption on the crystalline Nb_2O_5 particles. The Raman spectra in Figure 7 reveal that the 630 cm^{-1} band of the surface niobium oxide phase begins to shift towards the 690 cm^{-1} band of crystalline Nb_2O_5 above 19% $\text{Nb}_2\text{O}_5/\text{Al}_2\text{O}_3$ due to the presence of crystalline Nb_2O_5 particles. Thus, XPS, XRD, CO_2 chemisorption, and Raman all demonstrate that a monolayer of surface niobium oxide on alumina, ~180 m^2/g , corresponds to ~19% $\text{Nb}_2\text{O}_5/\text{Al}_2\text{O}_3$.

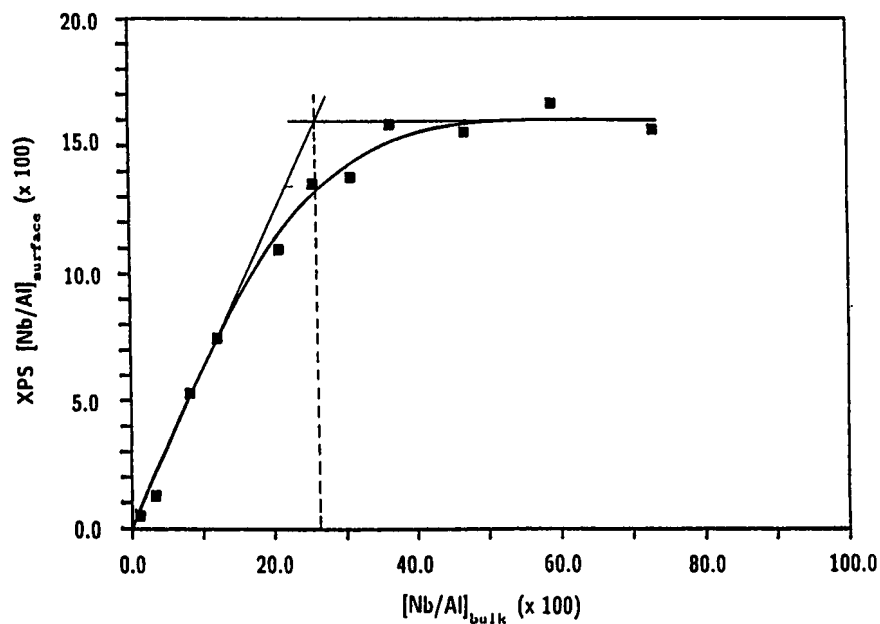


Figure 5: Raman shifts of Nb₂O₅/Al₂O₃(700°C) as a function of niobium oxide coverage.

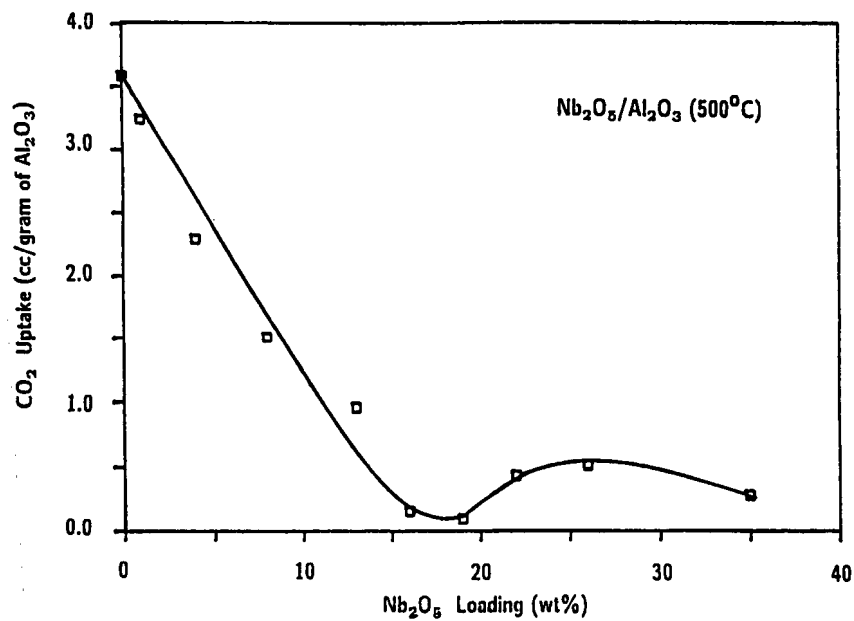


Figure 6: XPS intensity ratios of (Nb/Al)_{surface} as a function of (Nb/Al)_{bulk}.

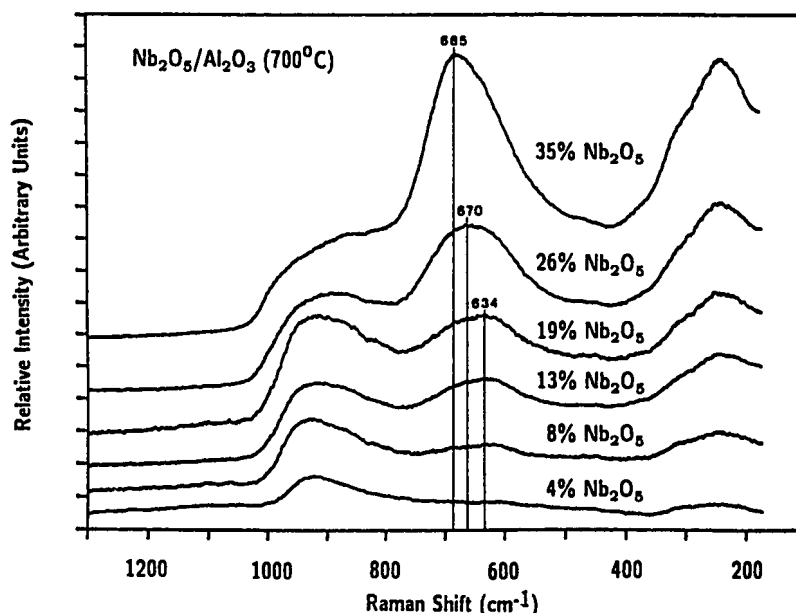


Figure 7: CO_2 uptake of $\text{Nb}_2\text{O}_5/\text{Al}_2\text{O}_3$ (500°C) as a function of niobium oxide coverage.

ACKNOWLEDGMENTS

The support of Niobium Products Company for this research project is gratefully acknowledged.

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ACIDIC PROPERTIES AND CATALYTIC ACTIVITIES OF NIOBIC ACID TREATED WITH PHOSPHORIC ACID

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SUMMARY

Phosphoric acid addition is effective for suppressing the crystallization and increasing the surface acidity of niobic acid (or niobium oxide), resulting in the enhancement of the catalytic activities for some acid-catalyzed reactions. The effects may be due to the formation of amorphous niobium phosphate on the surface.

INTRODUCTION

Niobic acid exhibits a considerably high acid strength even in the presence of water vapor, and, hence, is available as an effective catalyst for hydrations, dehydrations, alkylations with alcohols, and condensations. However, the acid amount on the niobic acid is relatively small, and the strong acidity is remarkably lost by heat-treatment at temperatures higher than 430°C, due to crystallization as Nb_2O_5 . For further development of niobic acid (or niobium oxide) as an industrial catalyst, these problems must be solved.

On the other hand, we have known that the addition of a small amount of bulky anions such as sulfate and phosphate ions is effective for the formation of stable TiO_2 (rutile) crystals (ref. 1). Furthermore, additions of some anions such as SO_4^{2-} and F^- were reported to enhance the surface acidities of certain metal oxides (ref. 2).

Accordingly, treatment effects with some acids, especially phosphoric acid, for suppression of crystallization and enhancement of surface acidity of niobic acid (or niobium oxide) was studied (ref. 3, 4) and some of these results are summarized in this article.

METHODS

Catalysts and their preparations

For the preparation of H_3PO_4 -treated niobic acid, niobic acid supplied by CBMM Comp. (AD-135) was immersed in 30 ml of a diluted

phosphoric acid solution (the concentration was adjusted at 0.05-1.0 mol.dm⁻³). The suspension of niobic acid was allowed to stand for 48 h, then the sample was evaporated to dryness in air at 120°C. The dried sample was heat-treated at temperatures ranging from 200 to 800°C. Before use as catalysts, the niobic acid (or niobium oxide) was fabricated to granules having size of 14-20 mesh.

Surface acidity and surface area

The surface acidities of niobic acid before and after acid-treatments were determined by NH₃ and pyridine adsorptions at various temperatures. The BET method (N₂ adsorption at -196°C) was applied for the determination of specific surface area.

XRD and XPS measurements

The XRD measurement was carried out using Geigerflex Diffractometer (Rigaku Denki Comp.). For the determination of the surface composition, XPS measurements were carried out by using ESCA 750 (Shimadzu Comp.).

TG-DTA measurement

For TG-DTA analysis, niobic acid before and after phosphoric acid treatment was heat-treated up to 800°C at a rate of 10°C per minute. For comparative purpose, niobic acid treated with sulfuric acid was also examined.

Catalytic reactions

As a typical acid-catalyzed reaction, in which water is formed as a by-product, cyclohexanol dehydration and benzene alkylation with methanol were selected. These reactions were carried out in an ordinary flow reactor under an atmospheric pressure.

RESULTS AND DISCUSSION

Effect on crystallization

As the full line in DTA pattern (Fig. 1) shows, a weak and dull peak is observed at around 200°C for the sample before acid-treatment. This peak is attributable to a partial dehydration, namely the change from 3Nb₂O₅·4H₂O to 3Nb₂O₅·H₂O (ref. 5). In addition, DTA for the untreated sample shows a sharp exothermic peak at around 550°C, nevertheless a change is little observed in TG (full line) during heat-treatment at from 300 to 800°C. Thus,

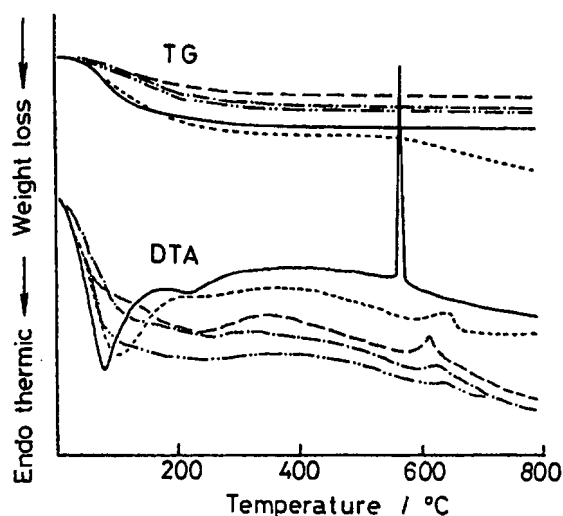


Fig. 1. TG-DTA patterns of niobic acid. — : Before treatment, ... : after treatment with H_2SO_4 (0.5 M), --- : after treatment with H_3PO_4 (0.25 M), - - - : after treatment with H_3PO_4 (0.5 M), - · - · : after treatment with H_3PO_4 (1.0 M).

the sharp peak observed in DTA is attributable to the transformation of amorphous to crystalline niobium oxide (ref. 6). This sharp peak was shifted to higher temperatures by the addition of sulfuric acid or phosphoric acid. Concurrently, the peak became less sharp and broadened with these acid-additions. In particular, the peak was little found for the sample treated with phosphoric acid of higher concentration (1.0 mol.dm^{-3}).

The effect of the phosphoric acid treatment for suppressing the crystallization was further confirmed by the fact that the XRD peaks of the sample treated with phosphoric acid were not so sharp even after heat-treatment at a high temperature such as 800°C . As a result of this suppression, the surface area of the niobic acid treated with phosphoric acid was fairly large even after heat-treatment at higher temperatures as shown in Fig. 2.

Effect on surface acidity

Similar to the surface area, the surface acidity of niobic acid (or niobium oxide) was increased by the acid treatment. The acid treatment was effective especially to lessen the drop in acidity during heat-treatment at higher temperatures as shown in Fig. 3.

When the amount of surface acid sites on the niobic acid before and after phosphoric acid treatment was determined by NH_3

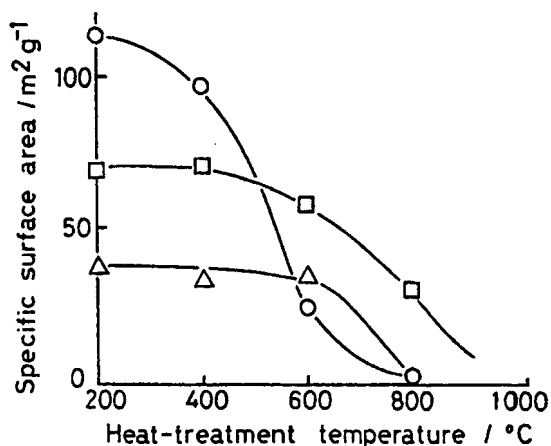


Fig. 2. Specific surface area of niobic acid. ○ : Before acid treatment, Δ : after treatment with H₂SO₄ (0.5 M), □ : after treatment with H₃PO₄ (0.5 M).

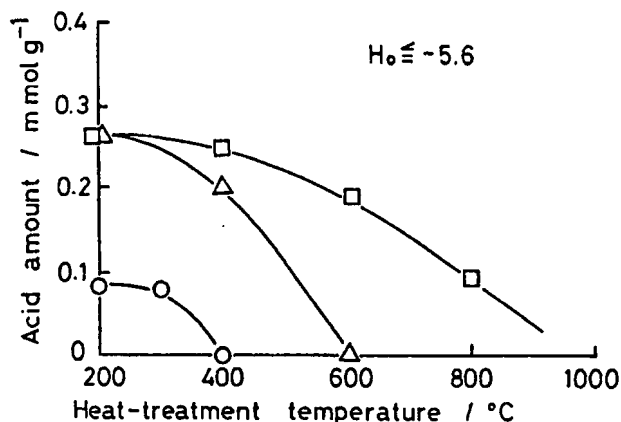


Fig. 3. Surface acidity of niobic acid before and after acid treatment. ○ : Before treatment, Δ : after treatment with H₂SO₄ (0.5 M), □ : after treatment with H₃PO₄ (0.5 M).

In Figs. 2 and 3, the concentration of phosphoric acid was adjusted at 0.5 mol.dm⁻³ to compare the treatment-effect with that using a strong acid, H₂SO₄. (H₂SO₄ is so strong that the acid of higher concentration may partly dissolve niobium oxide.)

adsorption, the amount per unit surface area or acid sites density increased with the phosphoric acid concentration. On the other

hand, the density determined by pyridine adsorption presented a maximum at a phosphoric acid concentration of 1 mol.dm^{-3} (Fig. 4). The difference between the acid sites densities determined by NH_3 and pyridine adsorptions may be resulted from the difference in

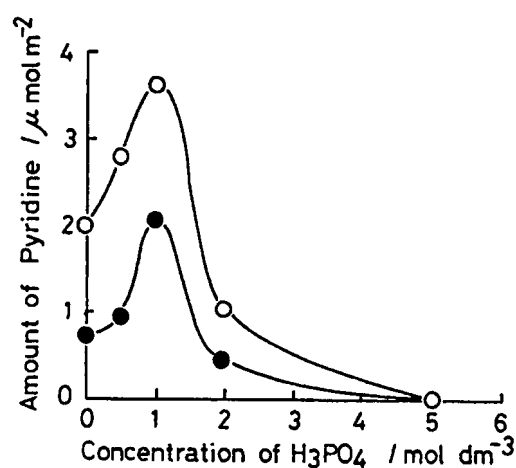


Fig. 4. Effect of H_3PO_4 concentration on surface acidity determined by pyridine adsorption. Adsorption temperature; O : 100°C , ● : 200°C .

the molecular sizes of these bases. That is, the smaller NH_3 molecules may penetrate the micro-pores of the surface layer formed by the phosphoric acid-treatment on the niobic acid, whereas the larger pyridine molecules may be unable to penetrate.

The surface layer is considered to be mainly composed of condensed phosphoric acid, especially for the sample treated with phosphoric acid of higher concentration (1.0 mol.dm^{-3}). In fact, the sample treated with 5.0 mol.dm^{-3} phosphoric acid was somewhat hygroscopic in contrast to that the sample treated with phosphoric acid of lower concentration (1.0 mol.dm^{-3}) was quite stable even in the moist air. Anyhow, the formation of the surface layer may be the reason for the decrease in the surface acidity observed for the sample treated with phosphoric acid of higher concentration (0.1 mol.dm^{-3}) (as shown in Fig. 4).

Surface compositions

The P/Nb atomic ratio in the surface layer of the phosphoric acid-treated sample linearly increased with the concentration of

phosphoric acid used for the surface treatment. The P/Nb ratio was fairly higher than the value calculated from the amount of phosphoric acid added to the niobic acid sample. The fact indicates that the P component is concentrated in the surface layer. In spite of the high concentration in the surface layer, the P component was little removed by a steam-treatment at 400°C for 3 h.

As Fig. 5 exhibits, the P/Nb atomic ratio in the surface layer was equal to 1 when the sample was treated with 1 mol.dm⁻³ acid solution. The fact suggests the formation of niobium phosphate, which is known to be Nb₂O₅.P₂O₅ or NbPO₅ (ref. 7), on the phosphoric acid-treated-sample surface. The niobium phosphate is amorphous, since the crystallized phosphate could not be detected by XRD analysis.

Possible interaction between Nb and P components

Fig. 6 indicates the XPS spectra of P, Nb, and O components in the surface layer of niobic acid treated with phosphoric acid of various concentrations. The number in the parentheses indicates the P/Nb atomic ratio. The peak position of P2p of the sample treated with phosphoric acid was, in general, shifted to the lower binding energy side compared to that observed for P₂O₅. The peak position for samples containing small amounts of the P component almost coincided with that for P³⁺ (134 eV) (ref. 8). The evidence suggests that P atoms might contribute to the withdrawal of electrons from the neighbouring Nb atoms; the contribution of individual P atoms might be more remarkable as the amount of phosphoric acid addition decreases. On the other hand, the peak due to Nb3d gradually shifted to the higher binding energy side upon increasing the amount of the phosphoric acid addition. The result suggested a withdrawal of electrons from Nb atoms by the phosphoric acid molecules added for the treatment. Thus, the electrons of the Nb atoms surrounded by a large amount of phosphate molecules might be drawn out to a greater extent; the largest shift to the higher energy side was observed for niobic acid containing the largest amount of the P component. The withdrawal of electrons should contribute to the enhancements of surface acidity and catalytic activities for acid-catalyzed reactions of the niobic acid.

Effect on catalytic activity

As is shown in Fig. 7, the catalytic activity of niobic acid

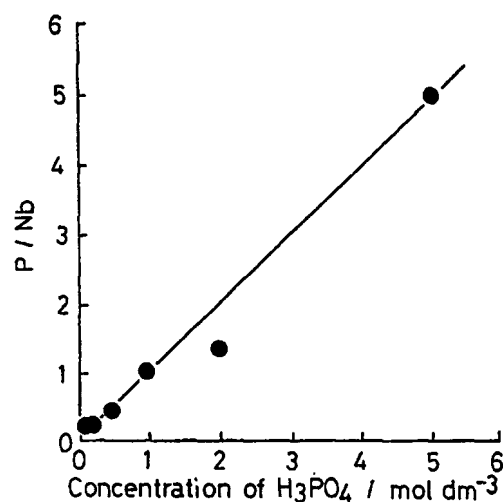


Fig. 5. Relationship between the concentration of H_3PO_4 used for the treatment and the atomic P/Nb ratio in the surface layer.

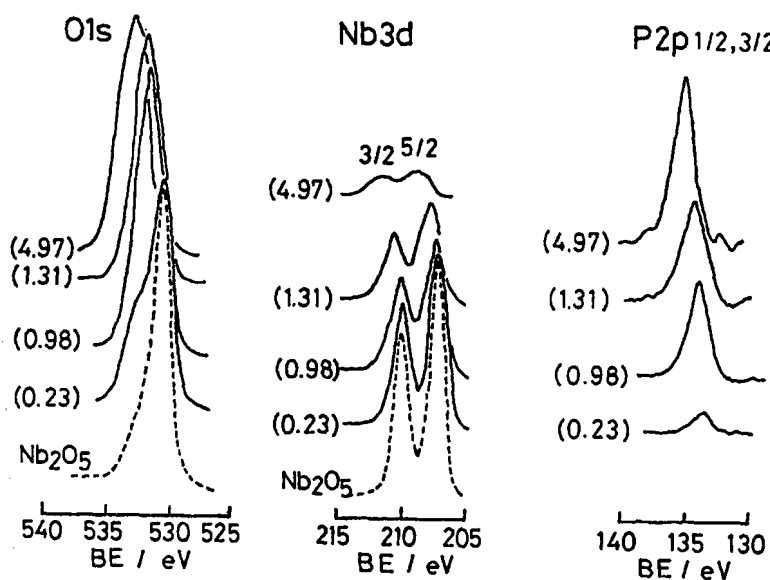


Fig. 6. XPS spectra for niobic acid before and after treatment with H_3PO_4 of various concentrations. Binding energy values were obtained by assuming the Cls peak position (due to contamination) as 285 eV.

in the cyclohexanol dehydration increased with a treatment using phosphoric acid (1 mol.dm^{-3}), and gradually decreased with increasing the heat-treatment temperature. The change of the catalytic activity corresponded to the change of the surface acidity.

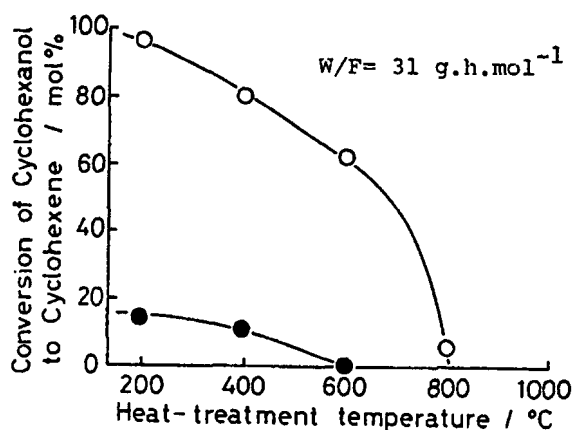


Fig. 7. Dehydration of cyclohexanol catalyzed by niobic acid before and after treatment with H_3PO_4 (1 M). ● : Before treatment, ○ : after treatment. Reaction temperature: 180°C .

In addition, the catalytic activity of niobic acid for the benzene alkylation was likewise increased by the phosphoric acid-addition. Thus, the catalytic activity for the alkylation was maximal when the niobic acid was treated with phosphoric acid having the concentration of 1 mol.dm^{-3} as is illustrated in Fig. 8. The result well corresponded to the change of the surface acidity with the concentration of phosphoric acid used for the treatment (Fig. 4). Hence, it is possible that the amorphous niobium phosphate formed on the niobic acid (or niobium oxide) surface is the active species promoting the alkylation.

Preparation and determination of surface acidity of amorphous niobium phosphate

In order to know the surface acidity of niobium phosphate directly, its preparation was first tried by various methods using different starting raw materials. As a result, it was found that the amorphous phosphate is most advantageously prepared by the addition of phosphoric acid to aqueous solution of $\text{K}_4\text{Nb}_6\text{O}_{17}$ (ref. 9).

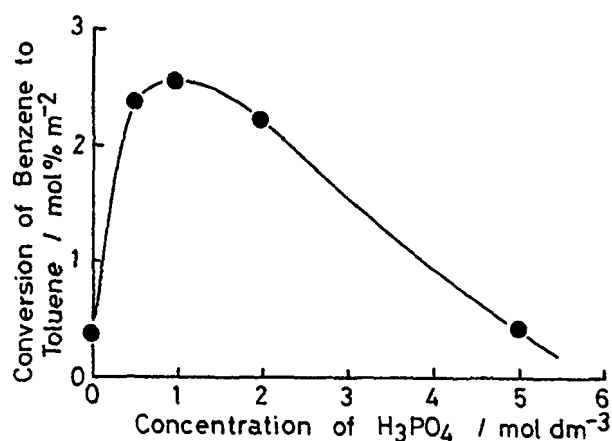


Fig. 8. Alkylation of benzene with methanol. Reaction temperature: $400^\circ C$; molar ratio of MeOH/benzene=0.3; heat treatment temperature of niobic acid: $400^\circ C$; pulse size: 2 l; catalyst: 50 mg.

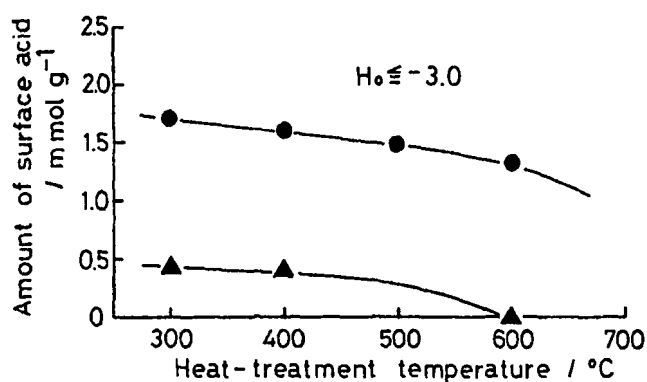


Fig. 9. Surface acidities of amorphous niobium phosphate and niobic acid at various heat-treatment temperatures. ● : Amorphous niobium phosphate; ▲ : niobic acid.

Then, the surface acidity of the amorphous phosphate was determined by amine titration, and compared to that of niobic acid. As a result, it was confirmed that the surface acidity is much higher than that of niobic acid. In addition, the large acidity is well retained up to higher temperatures (Fig. 10).

Furthermore, it was observed that the amorphous phosphate has a fairly large amount of stronger acid sites as shown in Fig. 10. The larger and stronger acidity may explain the pronounced acid property of niobic acid treated with phosphoric acid of appropriate

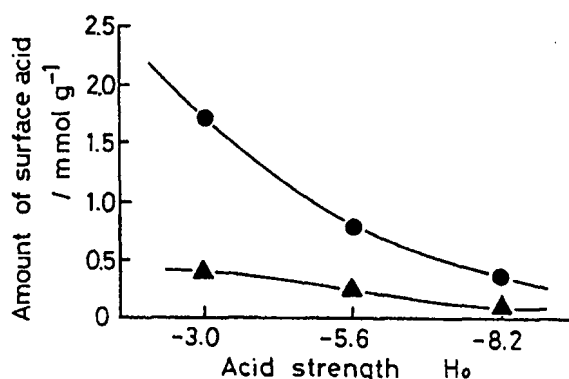


Fig. 10. Acid strengths of amorphous phosphate (●) and niobic acid (▲), heat-treated at 300°C

concentration (Figs. 3 and 4).

In contrast to the amorphous niobium phosphate, the crystalline phosphate prepared by other methods such as phosphoric acid-addition to niobium oxide dissolved by H_2SO_4 (ref. 10), HCl (ref. 11), or oxalic acid (ref. 9), exhibited only a little surface acidity and remarkably low catalytic activity for acid-promoted reactions.

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