  Bull. Chem. Soc. Jpn., 60, 37—41 (1987)

The Effect of Phosphoric Acid Treatment on the Catalytic Property of Niobic Acid

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(Received June 2, 1986)

The effects of the treatment of niobic acid with phosphoric acid, sulfuric acid, and hydrofluoric acid on its surface area, structure, acidic property, and catalytic activity have been studied. The treatment with phosphoric acid was found to be most effective for maintaining a large surface area and a large amount of strong acid sites and for preventing niobic acid from crystallizing even after the heat treatment at higher temperatures above 600 °C. The XPS study revealed that a large amount of phosphorous exists on niobic acid after high temperature heat treatment. In accordance with these results, niobic acid treated with phosphoric acid and heat-treated at higher temperatures exhibited high catalytic activities for methanol conversion and ethylene hydration, whereas the activities of niobic acid containing no phophoric acid were very low when heat-treated at high temperatures.

Recently, niobic acid ($Nb_2O_5 \cdot nH_2O$) is known to have a strong acidic property and catalytic activity towards acid-catalyzed reactions such as ethylene hydration,[1] esterification of acid with alcohols,[2] butene isomerization[3] etc. even on the heat treatment at lower temperatures (100—200 °C). However, on the heat treatment at higher temperatures (550 °C), niobic acid decomposes to become a crystalline niobium oxide and loses its acidic property and catalytic activity.[3]

On the other hand, it is known that the addition of SO_4^{2-} or F^- ions to a metal oxide such as Al_2O_3 or TiO_2 enhances the acidity of the metal oxide and that the addition of SO_4^{2-} prevents TiO_2 from changing to stable rutile crystals.[4]

Thus, in this study, the effect of the treatment of niobic acid with various acids, especially phosphoric acid, was examined for the purpose of strengthening the solid acidity of niobic acid even after the treatment at high temperatures. The conversion of methanol and the hydration of ethylene were tested to measure the effect of acid treatment on the catalytic activity of niobic acid.

Experimental

Catalyst Preparation. Niobic acid (AD-135) supplied by CBMM was dried in air at 120 °C for 6 h. For the preparations of acid-treated samples, niobic acid (10 g) was immersed in 30 ml of an acid solution prepared so as to have a given concentration (0.05, 0.25, 0.5, and 2.5 mol dm^{-3} of HF; 0.5 mol dm^{-3} of H_2SO_4; 0.25, 0.5, and 1 mol dm^{-3} of H_3PO_4). 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 calcined at various temperatures.

Surface Acidity and Specific Surface Area. The amount of surface acidic sites was measured by butylamine titration method, using various Hammett indicators. The BET method was used to measure the specific surface areas. Constant-volume adsorption of N_2 was carried out at 78 K for the sample having a particle size of 14—20 mesh.

TG-DTA, XRD, and XPS Measurements. For the measurement of TG-DTA, untreated and acid treated niobic acid, all dried at 120 °C, were used in an amount of 2.0 g each. The programmed temperature was raised at a rate of 10 °C min^{-1} up to 800 °C. The XRD experiments were done by using copper as the target and nickel as the filter. Some of the samples of untreated and acid treated niobic acid were subjected to XPS measurement for the surface composition after heat treatment at 400 °C or 600 °C. The Ar ion sputtering for 5 or 15 min was used to know the composition of several inner layers.

Methanol Conversion Reaction and Hydration of Ethylene. The methanol conversion was carried out at 400 °C, under normal pressure using a conventional flow reactor. One gram of catalyst, having a particle size of 14 to 20 mesh was fixed in the reactor and heat-treated in He stream at 400 °C for 1 h. The methanol feed was passed through a preheater at a constant rate of 1.8 ml h^{-1} by means of a microfeeder so that methanol was vaporized and led into the reactor by He carrier gas at a rate of 60 ml min^{-1}. The product gas was analyzed by gas chromatography. The reaction procedure of ethylene hydration was the same as reported previously.[3]

Results and Discussion

Surface Acidity. The acidity change of acid treated and untreated niobic acid after heating at various temperatures was summarized in Table 1. On the untreated niobic acid, strong acid sites of $H_o \leq -5.6$ appeared when samples were heat-treated at 200 or 300 °C. However, such strong acid sites were not found for the samples heat-treated at higher temperatures. In addition, the weaker acid sites of $1.5 \geq H_o > -5.6$ decreased with the rise of treatment temperature. The decrease of acid sites has been ascribed to the crystallization of Nb_2O_5.[3]

When niobic acid was treated with HF of concentration being 0.5 mol dm^{-3} or below, the amount of the weaker acid sites increased from 0.23 to 0.35—0.38 mmol dm^{-3}, whereas there was no change or somewhat decrease in the amount of the strong acid sites. However, the strong acid sites on HF treated sample remained after heat treatment at 400 °C in contrast with the case of untreated niobic acid. After

the treatment with HF of higher concentration, the acid sites on niobic acid decreased drastically.

If a niobic acid was treated with 0.5 mol dm^{-3} H_2SO_4, the acidity increased remarkably and the strong acid sites were retained even after the heat treatment at 400 °C. It is known that some metal oxides such as ZrO_2, TiO_2, and Fe_2O_3 show solid super acidity ($H_o \leq -12$) after the treatment with H_2SO_4 followed by the heat treatment at 500—600 °C.[5] However, on the surface of niobic acid, the strong acidity ($H_o \leq -5.6$) diminished after heating at 500—600 °C.

Figure 1 shows the surface acidity of niobic acid treated similarly with 1.0 mol dm^{-3} of phosphoric acid and then heat-treated at various temperatures. It is observed that the phosphoric acid treatment retains relatively large amount of strong acid sites. Surface treatment with 0.5 mol dm^{-3} of phosphoric acid enhances the surface acidity similarly to that with 1.0 mol dm^{-3} of phosphoric acid.

Figure 2 shows the relationship between the temperatures of heat treatment and the amounts of strong acid sites ($-5.6 \geq H_o > -8.2$) of niobic acid untreated or treated with acids. As obvious from this figure, the treatment with phosphoric acid differs from the treatment with other acids in that the strong acid amount is fairly retained at 600 °C and even 800 °C. As can be seen from a comparison of Fig. 1 with Fig. 2, the acid amount retained at 600 °C or higher temperature does not depend on the concentration of phosphoric acid.

As described above, the niobic acid treated with phosphoric acid does not lose strong acidity even after the heat treatment at high temperatures. This fact is considered to be due to the nonvolatile polyphosphate formed by the condensation of phosphoric acid on and near the surface of niobic acid. The ability of niobic acid to retain strong acidity at high temperature is not changed by the phosphoric acid concentration, and this fact indicates that a polyphosphate layer is formed in an amount enough to cover the full surface even when phosphoric acid is used at a relatively low concentration such as 0.5 mol dm^{-3}.

TG-DTA and XRD. TG-DTA was conducted to obtain an information about thermal stability of acid

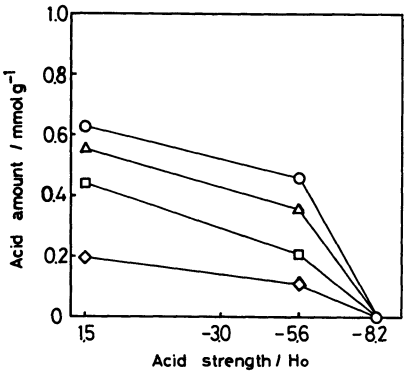

Fig. 1. Surface acidity of niobic acid treated with 1 mol dm^{-3} H_3PO_4.
Heat treatment temperature; ○: 200 °C, △: 400 °C, □: 600 °C, ◇: 800 °C.

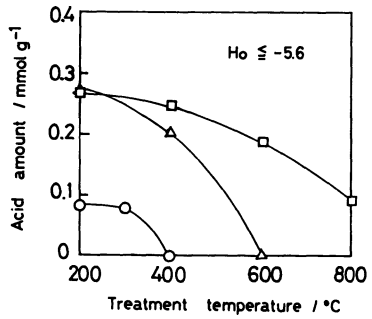

Fig. 2. Surface acidity of niobic acid before and after acid treatment.
○: Before treatment, △: after treatment with 0.5 mol dm^{-3} H_2SO_4, □: after treatment with 0.5 mol dm^{-3} H_3PO_4.

Table 1. Acid Amount on Niobic Acid Before and After Acid Treatment

Heat treatment temperature / °C	Acid amount on niobic acid/mmol dm^{-3}						
	Before acid treatment		Treated with HF of various concentration			Treated with H_2SO_4 of 0.5 mol dm^{-3}	
	LS[a]	S[a]	Concd / mol dm^{-3}	LS[a]	S[a]	LS[a]	S[a]
200			0.05	0.35	0.09		
	0.23	0.09	0.25	0.38	0.10	1.19	0.27
			0.5	0.38	0.04		
			2.5	0.10	0		
300	0.25	0.08					
400	0.13	0				0.42	0.20
500	0.10	0				0.35	0.05
600	0.03	0				0.15	0

a) LS: amount weaker acid ($1.5 \geq H_o > -5.6$) site. S: amount of strong acid ($-5.6 \geq H_o > -8.2$) site.

treated niobic acid. Figure 3 shows the TG–DTA patterns of the untreated niobic acid and phosphoric acid or sulfuric acid treated samples. At and near 200 °C, it shows a weak and dull endothermic peak. According to Sen et al., niobic acid has a composition of $3Nb_2O_5 \cdot 4H_2O$ at 150 °C and $3Nb_2O_5 \cdot H_2O$ at 300 °C.[6] Therefore, the peak around 200 °C is attributable to a partial elimination of water of crystallization. TG showed little change when untreated and H_3PO_4-treated samples were heated to temperatures ranging from 300 to 800 °C. However, DTA shows a sharp exothermic peak around 550 °C. This peak has been attributed to the transformation of niobic acid to crystalline niobium oxide.[3] The sharp exothermic peak near 550 °C is characteristic of niobium oxide. The crystallization of niobium oxide was prevented considerably by the addition of sulfuric acid or phosphoric acid. In DTA, the exothermic peak grew blunt and shifted to the higher temperature region. As found especially in H_3PO_4-treated samples, the effect becomes more remarkable with the increase in the treatment concentration. With a concentration of 1 mol dm^{-3} phosphoric acid, the exothermic peak is no longer observed. Sulfuric acid treatment also showed the similar effect, but TG showed the weight decrease at 600 °C or higher. This is probably due to the elimination of SO_3. Along with this elimination, the acidity of niobic acid rapidly decreased (See Fig. 2). In contrast, niobic acid treated with phosphoric acid did not show any weight loss due to the decomposition and retained the strong acid sites even after the heat treatment at high temperature.

In Fig. 4 are shown XRD patterns of untreated and acid treated niobic acid. After heating at 400 °C or below, samples showed only very broad peaks at about 30° (d=2.08 Å) and about 55° (1.67 Å). When heat-treated at higher temperatures, sharp peaks were observed on untreated niobic acid. The sample treated with sulfuric acid and heat-treated at 600 °C gave the peaks similar to those on untreated samples heated at 600 °C, but the peak strength was somewhat lower. At 800 °C, new peaks appear at 23.7° and 25.0°, but there is no change in main peaks. On the other hand, the diffraction peaks of the samples treated with phosphoric acid had quite low strength. Even after the heat treatment at 800 °C, the peaks were not so sharp. Thus, the treatment with phosphoric acid proves to be especially effective in preventing the crystallization of niobium oxide.

Surface Area. Samples untreated or treated with sulfuric or phosphoric acid were examined for the relationship between specific surface areas and heat treatment temperatures. As is shown in Fig. 5, the surface area of the untreated sample sharply drops between 400 and 600 °C. This decrease in surface area is due to the crystallization of niobium oxide occurring around 550 °C. Furthermore, the extremely small surface area observed at 800 °C suggests that the crystallization has been completed at this temperature. In the case of sulfuric acid treated niobic acid, the surface area was constant up to 600 °C, but drastically decreased after heating at 800 °C. The sample treated with phosphoric acid had lower surface area at 200 °C than that of the untreated niobic acid, but it showed the lowest extent of decrease with the rise of temperature. After heat treatment at 800 °C, the

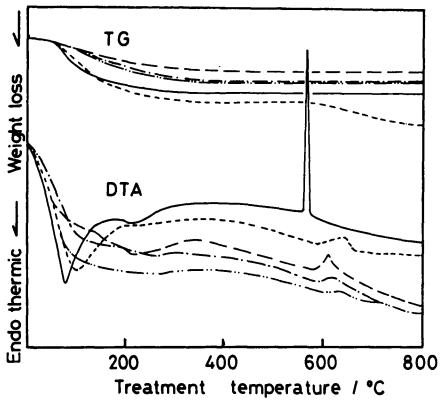

Fig. 3. TG–DTA patterns of niobic acid.
——: Before treatment, – – –: after treatment with 0.5 mol dm^{-3} H_2SO_4, — —: after treatment with 0.25 mol dm^{-3} H_3PO_4, —·—: after treatment with 0.5 mol dm^{-3} H_3PO_4, —··—: after treatment with 1.0 mol dm^{-3} H_3PO_4.

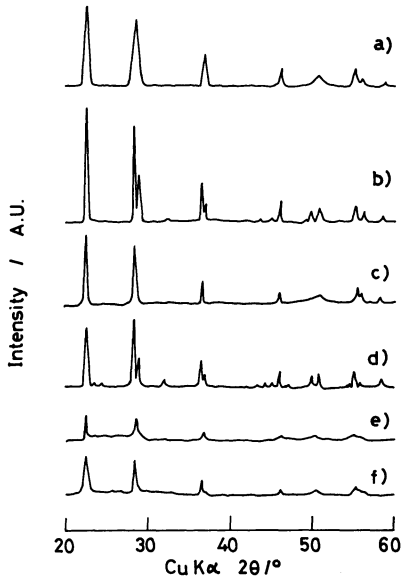

Fig. 4. XRD patterns.
a) Niobic acid heat-treated at 600 °C, b) niobic acid heat-treated at 800 °C, c) H_2SO_4-treated niobic acid, after heat-treated at 600 °C, d) H_2SO_4-treated niobic acid, after heat-treated at 800 °C, e) H_3PO_4-treated niobic acid, after heat-treated at 600 °C, f) H_3PO_4-treated niobic acid, after heat-treated at 800 °C. The concentrations of the H_2SO_4 and H_3PO_4 used for the treatment were 0.5 mol dm^{-3}.

sample retained a relatively large surface area of 33 $m^2 g^{-1}$. Thus, the effect of phosphoric acid treatment is remarkable to maintain the large surface area of niobic acid.

Surface Composition. The XPS study was made to obtain an information about surface composition of niobic acid. Surfaces of untreated and phosphoric acid treated samples were etched for 0, 5, and 15 min. In Table 2, the surface compositions determined by XPS are shown. The untreated sample gave a Nb/O atomic ratio of 27/73 regardless of heat treatment temperature. This ratio is roughly equal to the theoretical Nb/O value of Nb_2O_5 (29/71). After heating at 400 °C, the Nb/O ratio slightly increased as the time of Ar^+ etching became longer. After 15 min of etching, the observed value reached the theoretical value. On the other hand, after heating at 600 °C, the Nb/O ratio sharply increased along with the etching. This indicates that Nb atoms are regularly arranged on stable and strong grids and are difficult to eliminate on etching; therefore oxygen atoms are preferentially eliminated.

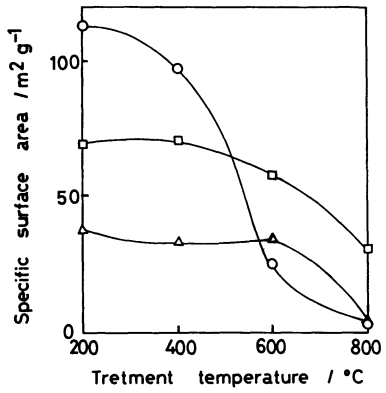

Fig. 5. Specific surface area of niobic acid.
○: Before acid treatment, △: after treatment with 0.5 mol dm^{-3} H_2SO_4, □: after treatment with 0.5 mol dm^{-3} H_3PO_4.

As regards the samples treated with phosphoric acid, the P/Nb ratio at 600 °C is slightly lower than that at 400 °C, indicating a possibility of the loss of P component and crystallization during the heat treatment at high temperatures. Even in this case, a P/Nb ratio close to 0.5 enables us to expect that a considerable part of surface layer will be covered with phosphoric acid (probably in the form of polyphosphate). Even when the sample was heat-treated at 600 °C, a relatively high P value of 6 atomic% is retained. This indicates that phosphoric acid penetrates to inner layers of niobic acid.

Catalytic Activity in Methanol Conversion. The product distribution of methanol conversion is shown in Table 3. Though the main product was dimethylether (DME), a considerable amount of methane formed over niobic acid heat-treated at 400 °C. After heating at 600 °C, which is higher than the crystallization temperature of niobium oxide, the activity decreased and especially methane formation was

Table 2. Surface Composition of Niobic Acid Before and After H_3PO_4-Treatment

Heat treatment temperature/°C	Ar^+ etching time/min	Composition/atomic/%		
		Nb	O	P
Before treatment				
400	0	27	73	
	5	28	72	
	15	29	71	
600	0	27	73	
	5	35	65	
	15	36	64	
After treatment with 0.5 mol dm^{-3} H_3PO_4				
400	0	11	19	70
	5	9	25	67
	15	8	25	68
600	0	9	20	70
	5	8	24	67
	15	6	30	63

Table 3. Results of Methanol Conversion Catalyzed by Niobic Acid Before and After Treatment with Phosphoric Acid

Heat treatment temperature/°C	Product distribution/mol/%[a]					
	CH_4	$CH_2{=}CH_2$	CH_3CH_3	$CH_3CH{=}CH_2$	DME[b]	CH_3OH
Before treatment						
400	32.4	0.8	0.7	0.4	45.6	20.1
600	8.1	0.1	0.1	0	65.8	25.9
After treatment with 0.5 mol dm^{-3} H_3PO_4						
400	8.1	0.3	0.2	trace	67.0	22.5
600	10.5	0.5	0.3	0.3	66.4	22.1

a) The reactions were carried out at 400 °C. The CH_3OH was fed to a conventional flow reactor containing 1 g of catalyst at a rate 1.8 ml h^{-1} through a preheater. b) DME denotes dimethyl ether.

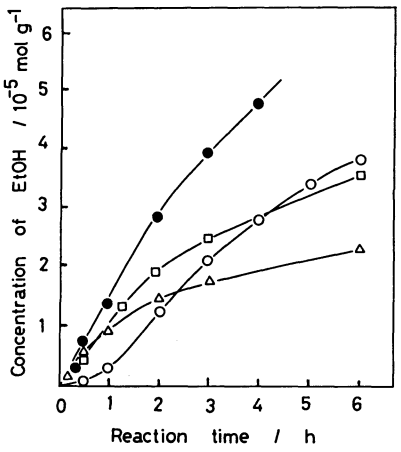

Fig. 6. Catalytic activity of niobic acid treated with 0.5 mol dm^{-3} H_3PO_4 for ethylene hydration.
○: Niobic acid, □: niobic acid treated with H_3PO_4, 1 st run, ●: niobic acid treated with H_3PO_4, 2 nd run (evacuated at 500 °C before the 2 nd run), △: solid phosphoric acid.
All these catalysts were heat-treated at 220 °C under evacuation for 1 h (for untreated or H_3PO_4-treated niobic acid) or about 5 min (for solid phosphoric acid) before use as a catalyst.

depressed.

On the other hand, the catalytic activity of niobic acid treated with phosphoric acid was not so sensitive to the heat-treatment temperature. Besides DME and methane, small amounts of olefin were formed in this reaction. The olefin formation was promoted more effectively by the niobic acid treated with phosphoric acid compared with the untreated sample after heat-treated at 600 °C. It is known that the olefin formation is promoted only by strong acid sites,[7] whereas the DME formation may be promoted by weak ones. So, the results described above suggest that strong acid sites should be formed and retained on niobic acid treated with phosphoric acid even after the heat treatment at higher temperature (600 °C).

Catalytic Activity in Ethylene Hydration. A gas-phase reaction was carried out in a circulation system at 220 °C to examine the catalytic activity of niobic acid treated with 0.5 mol dm^{-3} of phophoric acid in ethylene hydration reaction. The results obtained are shown in Fig. 6. For comparison, the previously reported results[1] obtained under the same reaction conditions for solid phosphoric acid and untreated niobic acid are also shown here. The untreated niobic acid has a higher catalytic activity than conventionally used solid phosphoric acid. It should be noted, however, that the activity is fairly low during the initial period of reaction. In contrast, niobic acid treated with phosphoric acid showed a high activity from the beginning. It is especially noted that, when the H_3PO_4-treated catalyst was heated at 500 °C in a vacuum, and then used in the reaction, the catalytic activity increased remarkably. This fact is in contrast to the case of untreated niobic acid which showed low activity when evacuated at 500 °C. Namely, the phosphoric acid treatment seems to be the reason for maintaining the catalytic activity even after the heat treatment at a high temperature such as 500 °C. In these ethylene hydration reactions, the heat treatments were carried out under evacuation, since they were attempted in the circulation system to use the niobic acid catalyst immediately after the treatment. However, it was confirmed that the heat treatment under atomospheric pressure affected the surface acidity and the catalytic activity of niobic acid, almost similarly to the heat treatment under evacuation. Thus, the H_3PO_4-treated catalyst has the advantage that the deactivated one can be recovered by heat treatment.

In the 1st-run reaction, the catalyst treated with 1 mol dm^{-3} phosphoric acid showed a higher activity than the sample treated with 0.5 mol dm^{-3} acid. However, in the second run reaction, the activity of the catalyst evacuated at 500 °C remained constant and independent of the concentration of phosphoric acid. As previously noted, the strong acid amount of niobic acid heat-treated at high temperatures remains roughly constant regardless of the concentration of phosphoric acid used for the treatment. Since the catalytic activity of H_3PO_4-treated catalyst is remarkably higher than that of solid phosphoric acid, it is speculated that phosphoric acid is not simply polymerized, but is condensed with niobium on the surface of niobium oxide and that for this reason, the H_3PO_4-treated catalyst works effectively to promote the reaction.

The authors are indebted to CBMM Ltd. for their providing the niobic acid samples and financial support on the present work.

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