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Surface Properties and Catalytic Activities of Niobic Acid Treated with Diluted Phosphoric Acid

Akito KUROSAKI, Tetsuhiro OKUYAMA, and Susumu OKAZAKI*
Department of Industrial Chemistry, Faculty of Engineering, Ibaraki University, Nakanarusawa-cho, Hitachi 316

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A surface treatment of niobic acid using about 1 mol dm^{-3} of phosphoric acid was effective for the enhancement of the surface acidity and the catalytic activity for some acid-catalyzed reactions such as cyclohexanol dehydration and alkylation of benzene with methanol. However, a treatment with phosphoric acid of higher concentration might form a deposit on the surface, which would prevent the penetration of reactants and/or products and, thus, decreased the catalytic activity of niobic acid. The P component added to the niobic acid was hardly removed by steaming at 400 °C, although it could be taken off by soaking in water at room temperature for twelve hours.

Niobic acid is known to exhibit a considerably high acid strength even in the presence of steam and, hence, to be available as an effective catalyst for hydration,[1] esterification,[2] or condensation,[3] which are to be performed in the presence of steam.[4] However, surface acidity of niobic acid remarkably decreases when it is heat-treated at temperatures higher than 400°C, possibly due to the crystallization which is known to be taken place above 435°C.[5] It was previously found that the decrease in the surface acidity lowered the catalytic activity of niobic acid for ethylene hydration and methanol conversion.[6] This limitation on the temperature restricts reaction conditions and the possibility for the reactivation of used catalysts. It was also found in a previous study[6] that the addition of a small amount of phosphoric acid is effective for preventing decreases in the surface acidity and the catalytic activity of niobic acid due to a heat treatment at temperatures higher than 400 °C. Furthermore, the phosphoric acid addition is even effective for increasing the surface acidity or enhancing the catalytic activity of the niobic acid heat-treated at lower temperatures. For uses of niobic acid as an industrial catalyst, the increase in the amount of acid sites seems essential; hence, the effects of a phosphoric acid addition on the surface acidity and on the catalytic activity for an acid-catalyzed reaction were investigated in more detail in this study. Especially, the durability of the P component was examined in terms of the change of the P content in the phosphoric acid-treated sample during a high-temperature (400 °C) steam treatment.

Experimental

Catalyst Preparation. Niobic acid (AD-135) supplied by CBMM was dried in air at 120 °C for 6 h. This material (10 g) was immersed in 30 ml of a phosphoric acid solution prepared so as to have a given concentration (0.05, 0.25, 0.5, 1, 3, or 5 mol dm^{-3} of H_3PO_4). The suspension of niobic acid was allowed to stand for 48 h; the sample was then evaporated to dryness in air at 120 °C. The dried sample was calcined at various temperatures ranging from 200 to 800 °C.

Surface Acidity and Specific Surface Area. The acidity of niobic acid before and after the acid-treatment was determined by adsorptions of ammonia and pyridine at various temperatures. The BET method was applied in order to measure the specific surface area. Constant-volume adsorption of N_2 was carried out at 78 K for samples having sizes of 14—20 mesh.

XRD and XPS Measurements. The XRD measurement was carried out using Geigerflex Diffractometer(Rigaku Denki) (target: Cu; filter: Ni). Some catalyst samples were heat-treated at 400 °C and then subjected to an XPS measurement (using Shimadzu ESCA 750) for the surface composition analysis. Also, ICP (Induction Combined Argon Plasma Emission Spectroscopy) was used to determine the change in the P content during a steam treatment.

Dehydration of Cyclohexanol and Alkylation of Benzene with Methanol. The dehydration of cyclohexanol was performed by using as a catalyst untreated niobic acid as well as niobic acid treated with 1 mol dm^{-3} phosphoric acid. The reaction was carried out at 180 °C under normal pressure using a conventional flow reactor. W/F was kept at 31.0 g · h · mol^{-1} for the catalytic dehydration. The alkylation of benzene with methanol was performed at 400 °C, using a pulse reactor. The pulse size and the catalyst weight were 2 μl and 50 mg, respectively. The molar ratio of methanol/benzene was adjusted at 3 for all the pulse reactions.

Results and Discussion

Surface Area. The surface area of niobic acid sharply dropped when the sample was heat-treated at temperatures above 400 °C, owing to the crystallization which should take place above 435 °C.[5] This decrease in the surface area was prevented by a treatment with 0.5—1.0 mol dm^{-3} of phosphoric acid, similarly to that observed previously.[6] However, treatments with phosphoric acid of higher concentrations were ineffective for the prevention of a decrease in the surface area, (Fig. 1). Especially, a treatment with 5 mol dm^{-3} phosphoric acid decreased rather than increased the surface area of the niobic acid heat-treated at 600 °C. It was possible that some niobium compound, such as niobium phosphate, was formed on the surface of niobic acid, although the XRD measurement did not show any peak ascribable to a newly formed compound on this sample.

Surface Acidity. The acidity changes of phos-

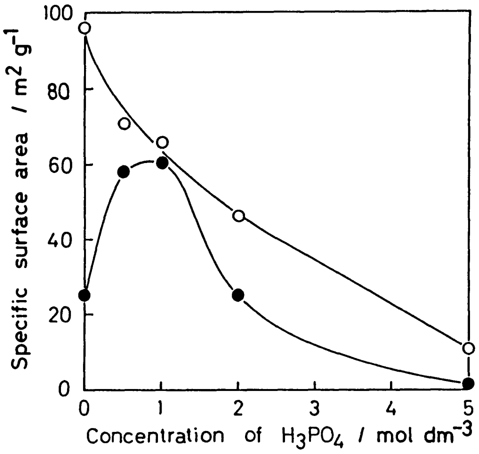

Fig. 1. Effect of H_3PO_4 concentration on specific surface area of niobic acid. Heat treatment temperature; ○: 400 °C, ●: 600 °C.

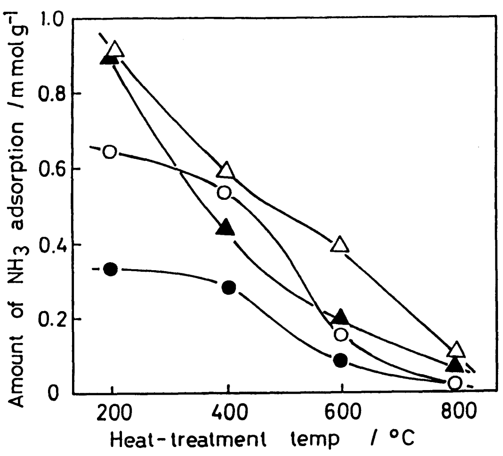

Fig. 2. Effect of heat treatment temperature on surface acidity of niobic acid before and after H_3PO_4 treatment. Concentration of H_3PO_4: 1.0 mol dm^{-3}; ○: adsorption at 100 °C on niobic acid before H_3PO_4 treatment; △: adsorption at 100 °C after treatment; ●: adsorption at 200 °C before treatment; ▲: adsorption at 200 °C after treatment.

phoric acid-treated and untreated niobic acid after heating at various temperatures were determined by the NH_3 adsorptions at 100 and 200 °C. As is shown in Fig. 2, the amount of NH_3 adsorbed at 100 and 200 °C on the acid-treated sample was larger than that adsorbed at a respective temperature on the untreated sample for all the heat-treatment temperatures ranging from 200 to 800 °C. Thus, the phosphoric acid treatment was effective irrespective of the heat-treatment temperature. Especially, adsorption amount of NH_3 at 200 °C was nearly equal to that of NH_3 adsorbed at 100 °C for the sample heat-treated at 200 °C. The evidence suggested that relatively strong acid sites were formed on the sample when the acid-treated sample was heated at a lower temperature such as 200 °C.

To determine the effect of the concentration of phosphoric acid used for the acid treatment on the

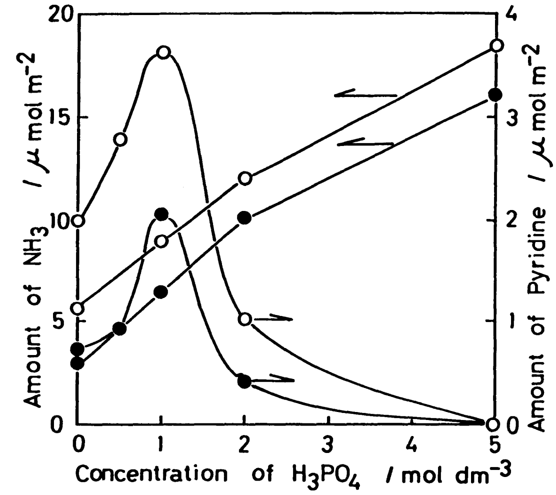

Fig. 3. Effect of H_3PO_4 concentration on surface acidity determined by NH_3 or pyridine adsorption. Ammonia and pyridine adsorptions were carried out by volumetric and gravimetric methods, respectively. Heat treatment temperature: 400 °C. Adsorption temperature: 100 °C (○) or 200 °C (●).

surface acidity of niobic acid, the adsorptions of NH_3 and pyridine on both treated and untreated niobic acid were attempted. The relationship between the amounts of NH_3 and pyridine per unit surface area and the concentration of used phosphoric acid is shown in Fig. 3. The amount of adsorption was similarly changed by changing the heat-treatment temperature, irrespective of the difference of the adsorption temperature. When the determination was carried out by the NH_3 adsorption, both the amounts per unit surface or densities, calculated for the adsorption temperatures of 100 and 200 °C on the niobic acid surface monotonously increased with the phosphoric acid concentration. On the other hand, the densities determined by the pyridine adsorption presented a maximum at a concentration of 1 mol dm^{-3}. This difference between acid site amounts (or densities) determined by NH_3 and pyridine adsorptions may be resulted from the difference in the molecular size of these bases. That is, the smaller molecules of NH_3 may penetrate through the micro pores of the surface layer formed by the phosphoric acid treatment on niobic acid, whereas the larger molecules of pyridine may be unable to penetrate. A similar phenomenon was observed by Itoh and Tada in their study on double adsorption of NH_3 and pyridine on Al_2O_3.[7] The surface possibly came to be covered more compactly as the concentration of the phosphoric acid used for the treatment became higher. On the other hand, the surface of niobic acid treated with less concentrated phosphoric acid might not be fully or less compactly covered by the compound newly formed on the surface. In such a state, the adsorption amount of pyridine was larger than that of NH_3 for the sample treated with phosphoric acid of lower concentration (0.5 and 1 mol dm^{-3}), since the basic strength of pyridine is higher than that of NH_3.[7-8] As a result of the two opposing effects, regarding the basic strength and the molecular size, respectively, a maximum was observed at a 1 mol dm^{-3} concentration of phosphoric acid for the adsorbed amount of pyridine (shown in Fig. 3).

Surface Composition and Structure. The atomic ratio of P/Nb in the surface layer of the catalyst determined by XPS linearly increased with increasing the concentration of phosphoric acid used for the treatment as shown in Fig. 4. The P/Nb ratio shown in the figure was considerably higher than the value calculated from the amount of phosphoric acid added to the niobic acid sample; for example, the value is calculated to be about 0.5 for the treatment with phosphoric acid of 1 mol dm^{-3}, but the experimental value is roughly 1. The evidence again indicated that the P component was concentrated in the surface layer. In spite of the concentration in the surface layer, the P component was slightly removed by a steam treatment at 400°C for 3 h (Fig. 5). The P component was partially removed by soaking in water with vigorous stirring at room temperature for 12 h.

XPS spectra regarding O, Nb, and P components in the surface layer of niobic acid samples containing various amounts of P component is shown in Fig. 6. The numbers in the parentheses indicate the atomic ratio of

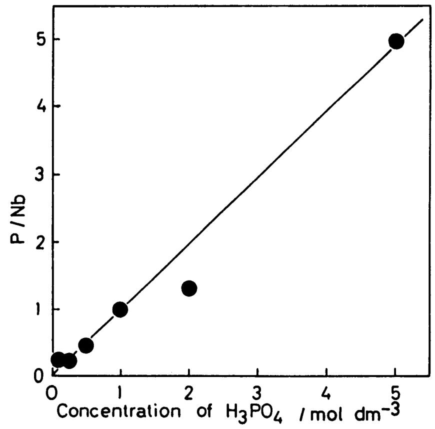

Fig. 4. Effect of H_3PO_4 concentration on atomic ratio P/Nb in surface layer of H_3PO_4-treated niobic acid.

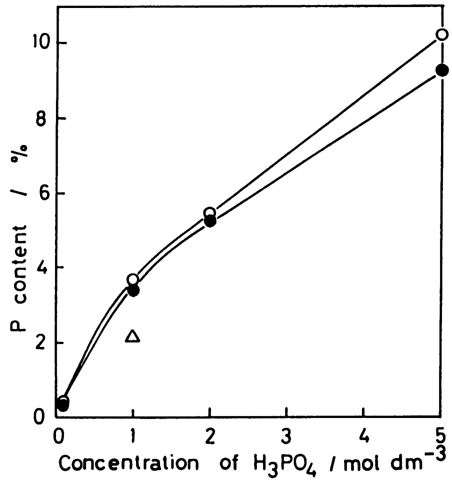

Fig. 5. Change of the P content of the acid treated sample during treatment with steam or water. ○: Untreated; ●: treated with steam. △: Treated with water at room temperature for 12h. The steam treatment was carried out at 400°C for 3h by using 106 m mol of steam per g of the niobic acid sample.

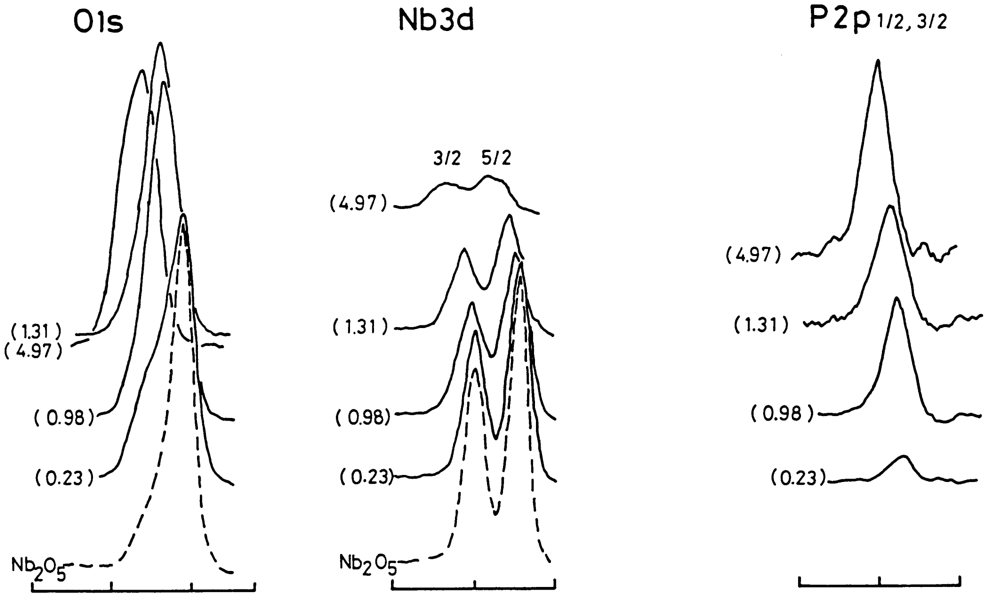

Fig. 6. XPS spectra for niobic acid before and after treatment with phosphoric acid. BE values shown here were obtained by assuming the Cls peak position due to contaminant carbon as 285 eV.

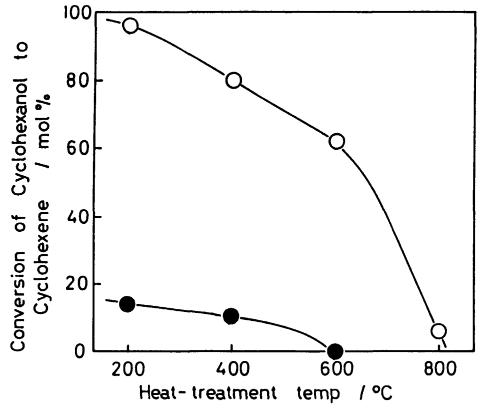

Fig. 7. Catalytic dehydration of cyclohexanol over niobic acid before and after treatment with H_3PO_4. Reaction temperature: 180 °C; W/F: 31.0 g·h·mol^{-1}. ●: Before treatment; ○: after treatment with 1.0 mol dm^{-3} H_3PO_4.

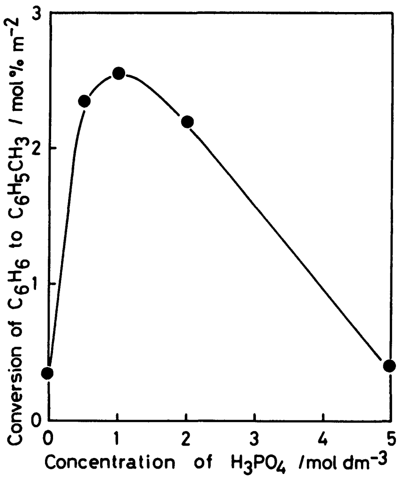

Fig. 8. Catalytic alkylation of benzene with methanol. Reaction temperature: 400 °C; molar ratio of MeOH/benzene=0.3; heat treatment temperature of catalyst: 400 °C; pulse size: 2 μl; catalyst weight 50 mg.

P/Nb determined by an analysis using XPS. The peak position of P2s for the sample treated with phosphoric acid was, in general, shifted to the lower BE side compared to that observed for P_2O_5 (135.8 eV, which was determined by taking Cls peak position of contaminant C as 285 eV).[9] The extent of the shift increased with decreasing the P content. Thus, the peak positions of samples having various atomic ratios of P/Nb are as follows: 135.8 (P_2O_5), 134.4 (P/Nb=4.97), 134.1 (1.31), 134.0 (0.98), and 133.7 (0.23) eV. The values for samples containing small amounts of the P component almost coincided with that for P^{3+} (134 eV).[9] 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 become more remarkable as the amount of phosphoric acid addition decreases. On the other hand, the peak due to Nb3d gradually shifted to the higher bonding energy side upon increasing the amount of the phosphoric acid addition. The result again 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 larger 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 (P/Nb=5). However, further details of the induction of electrons of Nb atoms, or the enhancement of the surface acidity due to Nb atoms are not clear at the present stage of this study.

Catalytic Activity in Cyclohexanol Dehydration. Similar to the surface acidity shown in Fig. 2, the catalytic activity of niobic acid in cyclohexanol dehydration, increased with a treatment using phosphoric acid, and gradually decreased upon increasing the heat-treatment temperature (Fig. 7). The change of the catalytic activity described above could be ascribed to a change in the surface acidity. Therefore, the addition of P component should contribute to an increase in the surface acidity, resulting in an enhancement in the catalytic activity in cyclohexanol dehydration.

Catalytic Activity in Alkylation of Benzene with Methanol. The conversion of the alkylation of benzene with methanol over niobic acid before and after a treatment with phosphoric acid of various concentrations is shown in Fig. 8. The catalytic activity of niobic acid, which was shown by the conversion of benzene to toluene, showed a maximum when the sample was treated with 0,5—1.0 mol dm^{-3} of phosphoric acid. As already shown in Fig. 3, a similar maximum value was also obtained for the amount of surface acidity, determined by pyridine adsorption, of H_3PO_4-treated niobic acid, when the phosphoric acid concentration was 1.0 mol dm^{-3}. This fact again suggests that the surface layers formed by the deposition of a phosphorus compound should absorb only small molecules such as N_2 (critical dimension: 3.0 Å[10]) and NH_3 (3.8 Å[10]). On the other hand, larger molecules such as benzene (6.8 Å[10]) might not be able to penetrate through the micro pores of the deposited compound and are, thus, little adsorbed on the H_3PO_4-treated niobic acid. Although the accurate molecular dimension of pyridine is not known, it is considered to be close to that of benzene. This seems to be the reason for obtaining a maximum at about the same concentration of the phosphoric acid to enhance the catalytic activity in the alkylation of benzene with methanol (Fig. 8) and to increase the surface acidity determined by pyridine adsorption (Fig. 3).

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