

Direct Synthesis of Methylisobutyl Ketone by Reductive Aldol Condensation

II. The Structure and Activity of Palladium-Zirconium Phosphate Catalyst

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A series of experiments was carried out to elucidate the relation between the surface structure and the activity of palladium-zirconium phosphate catalyst (Pd-ZrP cat) which has been effective for the direct synthesis of methylisobutyl ketone from acetone and hydrogen. In particular, the ionic state of Pd on zirconium phosphate (ZrP) was examined by means of spectrophotometric measurement of Pd ion species in aqueous phase, differential thermal analysis of Pd-ZrP gels, modified ion-exchange techniques and measurement of Pd particle size. It was found that Pd was introduced onto ZrP by ion exchange as divalent ammine-Pd cations. The structure of the Pd cations existing in a pH range 4.8-5.4 (selective catalyst for the direct reaction) could be concluded to be mono-, di- and/or triammine-Pd cation or their aquo-complex. The appearance of two exothermal peaks suggests the presence of two kind of Pd cation on ZrP. This is due to equilibrated distribution of ammine-Pd cations between strong and weak acid sites of ZrP.

INTRODUCTION

Recently, remarkable progress has been made in the preparation of supported metal catalysts. Several catalysts have been developed by loading supports with metals by means of ion-exchange technique (1). These catalysts contain very fine metal particles which are distributed uniformly on the supports. Many authors have studied the relation between specific reaction rates and particle sizes of the metal particles. The specific reaction rate is often unaffected by the particle size, but clearly affected in some cases (2-4). So, the relation between the structure and the activity of the catalyst should be investigated much more.

In our previous studies (5,6), the palladium-zirconium phosphate catalyst (Pd-ZrP cat) was newly found to be an effective catalyst acting as a bifunctional cat-

alyst directly to synthesize of methylisobutyl ketone (MIBK) from acetone and hydrogen. Moreover, it was confirmed that mesityl oxide was first formed by condensation of acetone on the acid sites of this catalyst and then converted to MIBK by its consecutive hydrogenation on the Pd particles. The main by-product was isopropyl alcohol formed by hydrogenation of acetone on the Pd particles.

It might be consequently suggested that the selectivity of the catalyst should greatly depend on the dispersion state of the Pd particles. According to the concept of Boudart (4), the activity of bifunctional catalyst in this study is expected to be structure-sensitive or, in other words, might be greatly dependent on the conditions to prepare the catalyst.

In this paper, the authors aimed to study the relation between the surface structure

of Pd-ZrP cat and its catalytic activity for the direct MIBK synthesis, by examining the influence of some conditions at the catalyst preparation.

EXPERIMENTAL METHODS

Preparation of the Catalyst

Pd-ZrP cat was prepared according to the standard method described in the previous paper (5). The course of the preparation is shown in Fig. 1. Zirconium phosphate (ZrP) was prepared by mixing the aqueous solutions containing equimolecular amount of H_3PO_4 and $ZrOCl_2$ in the presence of $PdCl_2$. Then the pH of the reaction mixture (slurry) was adjusted to 5.0 with 14% NH_4OH . The resulting precipitate was filtered and then washed with a dilute phosphoric acid solution, of which the pH value was approximately 5.0, and then dried at $110^\circ C$. The gel obtained (Pd-ZrP Gel) was calcined at $400^\circ C$ for 8 hr under a hydrogen stream to obtain the standard catalyst (Pd-ZrP cat).

The catalysts used in this study were prepared by changing the factors such as the pH to precipitate ZrP, the Pd quantity to be added and the reduction conditions.

Measurement of the Catalytic Activity

The flow reactor similar to that described in the preceding paper (5) was used to examine the activity of the catalyst for the direct MIBK synthesis. The catalyst in the form of 16-24 mesh particles (15 ml) was packed in the middle part of the reactor. The operating conditions were

as follows: reaction temperature, $120^\circ C$; reaction pressure, $20 \text{ kg/cm}^2 \text{ G}$; acetone LHSV, 4.0 hr^{-1} ; and hydrogen/acetone, 0.3-0.4 in molar ratio.

The effect of mass transfer under these conditions was found insignificant as elucidated previously (5). The reaction products was analyzed by gas chromatography. The by-products detected were isopropyl alcohol, mesityl oxide and diisobutyl ketone.

Spectrometry of Pd Ions

The absorption of an aqueous solution of Pd ions was measured at various pH values by use of Hitachi Model 323 spectrophotometer from Hitachi Ltd. The sample solution was prepared by dissolving $PdCl_2$ (1 g) in 1 N HCl (1.2 liters). The pH value of the solution was adjusted to the definite value with 14% NH_4OH .

The effect of phosphate ion on the absorption was also examined by adding $NH_4H_2PO_4$ to the solution.

Ion-exchange Technique

The following experiment was carried out to examine the possibility of coordination of phosphate ion with ammine-Pd cation at pH 5.0. Cation-exchange resin (Amberlite IR-120 B), packed in a column, was conditioned with an aqueous solution of $NH_4H_2PO_4$ (pH 5.0). An aqueous solution containing $PdCl_2$ and H_3PO_4 ($Pd = 0.00028 \text{ M}$, $PO_4^{3-} = 0.00056 \text{ M}$), the pH of which was adjusted to 5.0 with 14% NH_4OH , was passed through the column. The resin was then washed with an aqueous solution (pH 5.0) containing a small amount of $HClO_4$. The Pd cations held in the resin were eluted out with 1 N HNO_3 , and the palladium, chloride and phosphate ions in the elute were quantitatively determined.

Moreover, in order to clarify the state of ammine-Pd cation combined with ZrP, introduction of the ammine-Pd cation into a dried gel of ZrP in the hydrogen form was

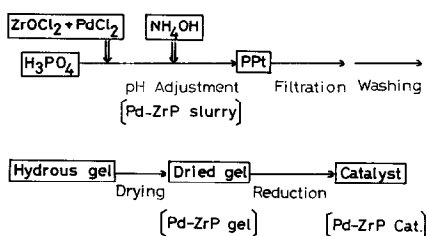


FIG.1. Flow diagram for the catalyst preparation.

examined. ZrP ($\text{PO}_4/\text{Zr} = 1$) was precipitated by reacting ZrOCl_2 and H_3PO_4 in the absence of PdCl_2 , washed repeatedly with water completely to remove chloride ion, and dried at 110°C . The finely divided particles of the dried gel were added to an aqueous solution of ammine-Pd cation (pH 5.0), and allowed to stand for 20 hr at room temperature. The aqueous solution of ammine-Pd cation was prepared by adding 14% NH_4OH to 1 N HNO_3 solution of PdCl_2 . Then, the chloride and palladium ions remaining in the aqueous phase were determined.

Chemical Analysis

The phosphate anion and ammine-Pd cation in an aqueous solution were determined by colorimetry, respectively, using phosphovanado-molybdic acid and *p*-nitrosodimethyl aniline as the chelating reagents. Metallic Pd on the catalyst was determined by fluorescent X-ray analysis. Chloride ion was determined by titration with 0.1 N AgNO_3 .

Thermal Analysis

The differential thermal analysis of Pd cations (Pd^{2+} and ammine-Pd cations) combined with ZrP was carried out by use of a differential thermal analyzer Model YGSD from Rigaku Denki Co. The dried powder (20 mg) of Pd-ZrP gel was heated under an aerobic atmosphere at the rate of $10^\circ\text{C}/\text{min}$ using α -alumina as a reference.

Measurement of Surface Area

The specific metal surface area of Pd-ZrP cat was measured by using the volumetric CO adsorption apparatus similar to that described by Scholten and Montfoort (7). The sample used was 1–2 g in each run. After evacuation with a diffusion pump at 300°C for 5 hr and then keeping Pd-ZrP cat under a CO pressure of 45–50 mm Hg for 16 hr, the amount of CO chemisorbed onto the catalyst was measured at 20°C . It was also observed that a considerable amount of CO was

chemisorbed onto ZrP without Pd. Then, the amount of chemisorbed CO on the Pd particles were obtained by subtracting the amount of chemisorbed CO on ZrP itself from that on Pd-ZrP cat. The specific surface area of the Pd particles was calculated with respect that 1 cm^3 (NTP) CO was able to cover the Pd surface area of 3.2 m^2 as done by Scholten and Montfoort (7). The mean particle size \bar{d} (\AA) was calculated as follows: $\bar{d} = 6/s \cdot \rho$, where ρ was the density of Pd ($\rho = 12.02$), and s was the specific surface area. The other methods such as X-ray line-broadening and electron microscopy were unsuccessful to measure the Pd surface area.

The surface area of Pd-ZrP catalyst was determined by the BET method with nitrogen.

Measurement of Acidity

ZrP gels were prepared according to the procedure for preparing the catalyst except for the absence of PdCl_2 . The white powder of the dried ZrP gel (100–200 mesh) was calcined at the definite temperature under a stream of dry air. The powder obtained was titrated in benzene with *n*-butylamine as done by Benesi (8). Color test was done by transferring the dried powder (0.5 g) into a 25 ml stopped flask, adding 10 ml of dry benzene, and two drops of 0.1% benzene solution of the indicator, dicinnamal-acetone ($\text{p}K_a = -3.0$), or benzalacetophenone ($\text{p}K_a = -5.6$). A 0.1 N benzene solution of *n*-butylamine was added dropwise to the flask from a pipet. The flask was allowed to stand for a few days to accomplish the titration. Furthermore, the end-point was checked by adding a drop of 0.1 N benzene solution of trichloroacetic acid.

RESULTS AND DISCUSSION

Effect of the pH Value in the Catalyst Preparation

First, ZrP was precipitated by mixing the aqueous solutions of H_3PO_4 and

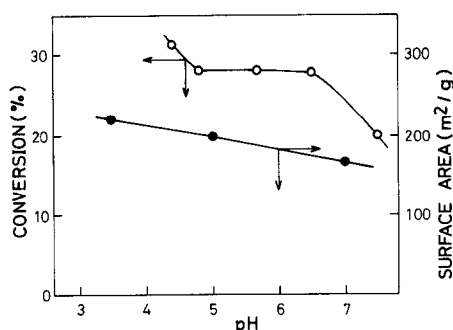


FIG. 2. Relations between pH and activity and surface area.

ZrOCl₂ in the presence of PdCl₂. The brown solution of the resultant mixture was strongly acidic owing to the HCl from ZrOCl₂. When the pH of the solution was raised to about 4.4 with 14% NH₄OH, the solution turned almost colorless and the Pd content in the aqueous phase sharply decreased with the slight increase in the pH value above 4.4. At pH 4.8, the color disappeared completely.

Considering that ZrP is an inorganic cation-exchanger even in hydrous state, these facts suggest that at pH less than 4.4, Pd ions exist in the form of brown chloro-Pd anions in the presence of the chloride ions, and consequently they are incapable of combining with the ion-exchange sites of ZrP, whereas the anions react with ammonia at pH 4.8 to form colorless ammine-Pd cations which are readily ion exchanged into the ZrP precipitate.

Figures 2 and 3 show the change in the catalytic activity and the surface area with

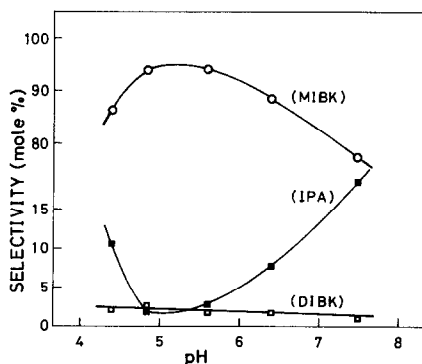


FIG. 3. Effect of pH on the product composition.

TABLE I
PALLADIUM PARTICLE SIZE OF
Pd-ZIRCONIUM PHOSPHATE^a

pH at catalyst preparation	Pd content (wt%)	Reduction		Av Pd particle size (Å)
		Temp (°C)	Time (hr)	
5.2	0.43	400	8	26
5.2	0.51	400	8	24
5.2	0.72	400	8	42
5.2	1.60	400	8	62
4.4	0.38	400	8	105
7.0	0.43	400	8	44
5.2	0.43	300	8	14
5.2	0.43	500	8	60

^a The average of chemisorbed CO on pure zirconium phosphate was 0.125 cc/g (NTP).

the pH value of the slurry. The conversion of acetone decreased with an increase of the pH value and this can be explained in terms of the decrease in the surface area of the catalyst. The selectivity for MIBK was as high as 94 mole% with the catalyst prepared in the pH range 4.8–5.6 and much decreased out of this pH range owing to the remarkable formation of isopropyl alcohol by simultaneous hydrogenation of acetone. The above dependence of the selectivity on the pH value is probably due to the change in the dispersion state of the Pd particles on ZrP.

Table I shows the average sizes of Pd-ZrP cat. The absolute values must be viewed with reserve, because a considerable amount of absorbed CO was observed with ZrP itself. However, these values are meaningful enough for the purpose of relative comparison. As to the effect of the pH value of the slurry, the smallest value of Pd particles size (26 Å) was obtained with the catalyst prepared at pH 5.2, while sintering of Pd metal was often observed at pH out of the pH range 4.8–5.6. Consequently the development of metallic Pd and its sintering degree may depend not only on reduction conditions but also on the initial structure of the Pd cations (Pd²⁺ and ammine-Pd cations) combining with ZrP of which the structure may be affected by the pH value of the slurry.

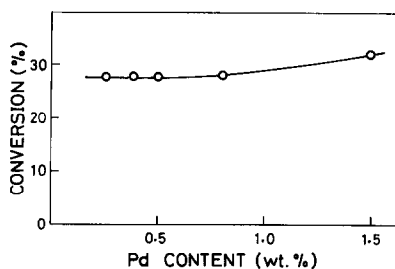


FIG. 4. Effect of Pd content on the conversion of acetone.

Effect of Pd Content in Catalyst

The effects of the Pd content on the catalytic activity are shown in Figs. 4 and 5. Both the amounts of isopropyl alcohol and diisobutyl ketone were markedly changed with the Pd content, whereas the conversion of acetone did not appreciably change. The amount of isopropyl alcohol increased with the increase in the Pd content. This is probably due to the increase in the sintering degree of the Pd particles, which may promote the hydrogenation of acetone (Table 1). It can be reasonably explained that the decrease in the Pd content resulted in increasing amount of diisobutyl ketone. Namely, further condensation of MIBK with acetone to diisobutyl ketone was promoted to some extent owing to the decrease in the surface concentration of the active sites for the hydrogenation, and on the other hand, the hydrogenation rate of mesityl oxide was depressed. These facts indicate that the

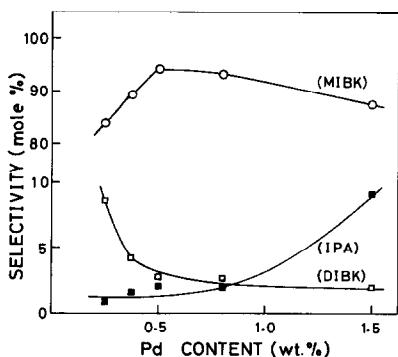


FIG. 5. Effect of Pd content on the product composition.

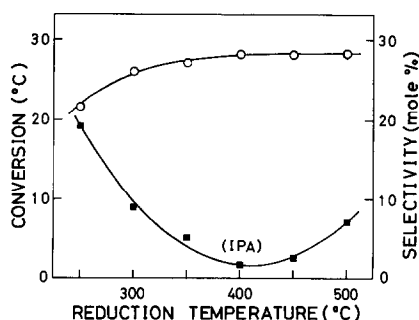


FIG. 6. Effect of reduction temperature upon the acetone conversion and the selectivity for isopropyl alcohol; treatment time, 8 hr.

optimum Pd content with respect of the surface concentration of the acid sites should be chosen for the selective formation of MIBK. The best result was obtained at the Pd content of 0.5 wt%.

Effect of Reduction Conditions

ZrP ion-exchanged with ammonium ions and ammine-Pd cations should be calcined under a reducing atmosphere to yield an effective catalyst having the acid sites and the metallic Pd particles. The course of both the formation of the acid sites and the development of the metallic Pd particles are shown below.

Figure 6 shows the effect of the reduction temperature on the catalytic activity. Figure 7 shows the change in acidities of the dried ZrP gel after calcination at various temperatures in a stream of dry air. When the reduction temperature was below 350°C, the conversion of acetone

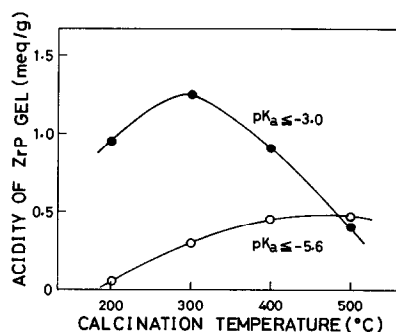


FIG. 7. Acidity of ZrP gel against calcination temperature; treatment time, 6 hr in a stream of air.

became lower and isopropyl alcohol was produced much more. Evidently, the thermal decomposition of the ammonium ions combining with ZrP is insufficient to yield the effective acid sites under such milder conditions of calcination. On the other hand, ammine-Pd cations are easily decomposed to result in the metallic Pd particles with liberation of ammonia, and consequently the hydrogenation of acetone may be favored in comparison with the condensation. Moreover, the reduction treatment at the temperature above 450°C is not preferable, because the amount of isopropyl alcohol appreciably increases. This may be understandable in terms of the sintering of the metallic Pd particles (Table 1).

By comparing the conversion curve in Fig. 6 with the acidity curve at $pK_a - 5.6$ in Fig. 7, it is supported that the sites with about $pK_a - 5.6$ might be effective for the condensation of acetone. Thus the relatively strong acid site is probably effective for the condensation of acetone, as presumed by the fact that a cation-exchange resin with sulfonic acid group was useful for the selective condensation of acetone to mesityl oxide (9). However, no distinct comparison is possible here.

Ionic State of Pd on ZrP

Since the pH value of the slurry, in which the Pd cations (Pd^{2+} and ammine-Pd cations) are ion exchanged with ZrP, considerable influences the selectivity of the resulting catalyst, the change in the structure of the Pd cations with the pH value of the slurry should be elucidated. Figure 8 shows the spectral change of an aqueous $PdCl_2-HCl$ system with the amount of ammonia added. The absorption peaks at 476, 420, 380 and 296 nm are characteristic for $PdCl_6^{4-}$, $PdCl_4^{2-}$, Pd^{2+} and $Pd(NH_3)_4^{2+}$, respectively (10). The result clearly indicates that the ionic forms changed from $PdCl_6^{4-}$ to $Pd(NH_3)_4^{2+}$ in the above order, depending on the change in

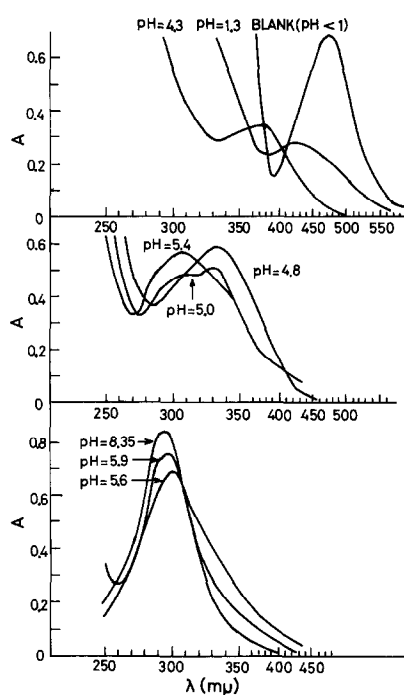


FIG. 8. Absorbance of $PdCl_2-HCl-NH_4OH$ system vs wave length as a function of pH.

the pH value of the system. The absorption maximum is observed between 300 and 340 nm in the pH range 4.8–5.4. This suggests the existence of some intermediate ion species such as mono-, di- and triammine-Pd cations.

By the standard method of catalyst preparation mentioned above, there still remains a small amount of the phosphate ion in the slurry where the protons of the acidic sites of ZrP are replaced with the Pd cations. The effect of the phosphate ion on the complex formation of the Pd ion was examined by adding ammonium phosphate to the $PdCl_2-HCl$ or $PdCl_2-HCl-NH_4OH$ solution. Figure 9 shows that no spectral change by the phosphate ion was observed at pH either below 4.3 or above 5.9. At pH 4.8, however, the spectrum changed significantly by the addition of the phosphate ion. Figure 10 shows the spectral change of the Pd cations with the concentration of phosphate at pH 5.2. The

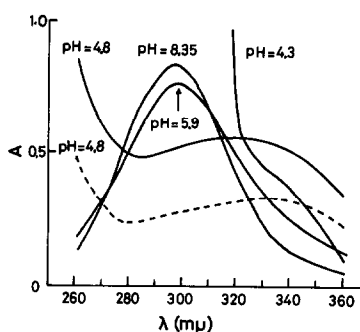


FIG. 9. Absorbance of $\text{PdCl}_2\text{-HCl-NH}_4\text{OH}$ -phosphate system vs wave length as a function of pH: (—) before addition of phosphate ions (Pd , 0.00028 mol; PO_4 , 0.00028 mol); (---) after addition of phosphate ions. No changes in absorbance with phosphate ions were observed at a pH of 4.3, 5.9 or 8.35.

maximum absorption at 300–340 nm shifts a little, while the absorbance at the absorption peak (near 300 nm) decreases with the increase in the concentration of the phosphate ion. The interaction between the phosphate ion and the Pd ions such as PdCl_6^{4-} , PdCl_4^{2-} , Pd^{2+} or $\text{Pd}(\text{NH}_3)_4^{2+}$ seems insignificant except in the pH range 4.8–5.4 in which the various types of ammine–Pd cations are formed. The effect of the phosphate ion in the above pH range (4.8–5.4) may suggest some interaction of the phosphate ion with the Pd cations.

In order to investigate the ionic state of Pd in an aqueous system of $\text{PdCl}_2\text{-HCl-NH}_4\text{OH-H}_3\text{PO}_4$ in the pH range 4.8–5.4,

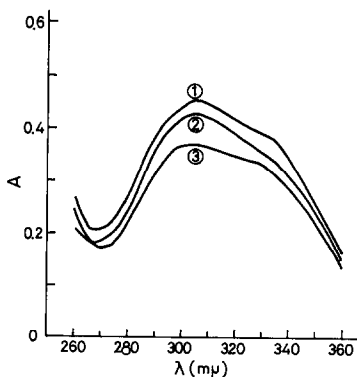


FIG. 10. The change in absorbance at pH of 5.2 with the added amount of ammonium phosphate: (1) Pd , 0.00056 mol; PO_4 , 0.00000 mol; (2) Pd , 0.00056 mol; PO_4 , 0.00056 mol; (3) Pd , 0.00056 mol; PO_4 , 0.00118 mol.

the introduction of the Pd cations into some ion-exchange resins was examined. By the addition of anion-exchange resin (Amberlite IRA-410, chloride form) to the same solution as shown in Fig. 10, no spectral change was observed. On the other hand, when cation-exchange resin (Amberlite IR-120B, hydrogen form) was added, the absorption of the solution completely disappeared.

Moreover, the possibility of coordinating the phosphate ion with the Pd cations at pH 5.0 was examined by using Amberlite IR-120B, packed in a column. More than 95% of Pd was recovered from the resin, while neither the phosphate ion nor the chloride ion was detectable in the eluate. This observation indicates that the Pd cations combined with the cation-exchange resin contain neither the phosphate ion nor the chloride ion as their components. Therefore, the effect of the phosphate ion on the absorbance of the aqueous solution of the Pd cations in the pH range 4.8–5.2, shown in Figs. 9 and 10, is probably understood in terms of some interaction rather milder than coordination between the phosphate ion and the Pd cations.

Moreover, in order to clarify the state of the ammine–Pd cation combined with ZrP, the introduction of the Pd cations into ZrP (H^+ form) in the $\text{PdCl}_2\text{-NH}_4\text{OH}$ system at pH 5.0 was examined, as shown in Fig. 11. Evidently, almost all of the Pd cations was introduced into ZrP, whereas all of the

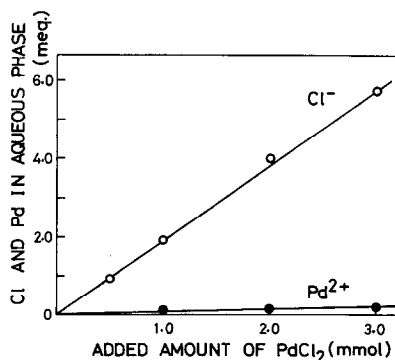


FIG. 11. Introduction of Pd cations into ZrP gels.

counter chloride anion remained in the aqueous phase. The result indicates that the Pd cations were introduced into ZrP by ion-exchange as divalent ammine-Pd cations which included no Cl atom in their components. The solid ZrP particles containing the Pd cations thus obtained were calcined under a hydrogen atmosphere to yield the efficient catalyst which was as highly selective as that obtained by the standard method.

Accordingly, it can be concluded that the Pd cations are introduced into ZrP by ion exchange as the divalent Pd cations such as Pd^{2+} , $\text{Pd}(\text{NH}_3)_4^{2+}$ and so on. The structure of the Pd cations combining with ZrP depends on the amount of ammonia added to the system. Considering the absence of coordination between the phosphate ion and the Pd cations, the structure of the intermediate Pd cations in the pH range 4.8–5.4 in the presence of ammonia could be concluded to be mono-, di- and/or triammine-Pd cations $[\text{Pd}(\text{NH}_3)_n]^{2+}$, $n = 1, 2$ or 3 , or their aquo-complex $[\text{Pd}(\text{NH}_3)_n(\text{H}_2\text{O})_{4-n}]^{2+}$, $n = 1, 2$ or 3 .

Thermal Change of the Pd Cations Combined with ZrP

By thermal treatment under a hydrogen atmosphere at about 400°C , the Pd ammine cations combined with ZrP can be decomposed and reduced into finely dispersed metallic Pd, which catalyzes the reduction of mesityl oxide to MIBK. At the same time, the acid sites of ZrP which release the Pd cations and ammonia molecules are regenerated and catalyzed condensation of acetone to mesityl oxide. The acid sites are also regenerated by thermal decomposition of ZrP (NH_4^+ form) (Fig. 12). Since the metallic Pd particles are also catalyzed the reduction of acetone to isopropyl alcohol, their dispersion state on ZrP should greatly influence the selectivity of the catalyst. The susceptibility of the Pd cations to be reduced to the metallic state and the dispersion state of the resulting Pd particles on ZrP may be significantly af-

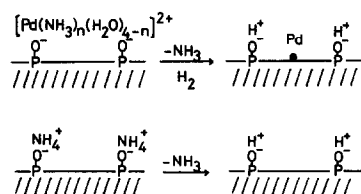


FIG. 12. Schematic diagram showing formation of acid site on Pd-ZrP catalyst.

ected by both the initial structure of the Pd cations and the acid strength of the ion-exchange sites of ZrP to be combined with the cations. Consequently, the pH value of the slurry in the catalyst preparation is one of the most important factors to control the activity of the catalyst, and this fact may be explained in terms of the pH effects on both the structure of the Pd cations and their distribution state on the acid sites having various acid strengths.

In order to clarify the pH effect on the state of the Pd cations combined with ZrP, the thermal change of ZrP containing the Pd cations was examined.

Figure 13 shows the differential thermograms of some typical dried Pd-ZrP gels which were prepared at various pH values. Figure 14 illustrates the effect of the content of the Pd cations on the thermal change of the dried Pd-ZrP gel prepared at pH 5.2. The shape and the number of the exothermal peak were changeable with such conditions to prepare the catalyst as the procedures of washing and filtration of the hydrous gel, the pH value of the slurry and the Pd content. As shown in Figs. 13 and 14, either single or double exothermal change was observed in each thermogram in the temperature range 270 – 400°C except in that of the ZrP gel without Pd, indicated in Fig. 13e. It was confirmed that each exothermal change was ascribed to oxidation of Pd cations to PdO. Since the single exothermal peak is observed about all the samples containing the ammine-Pd cations prepared at pH 5.2 (Figs. 13b and 14a, b and c, thermal change due to oxidative liberation of ammonia molecules from the Pd

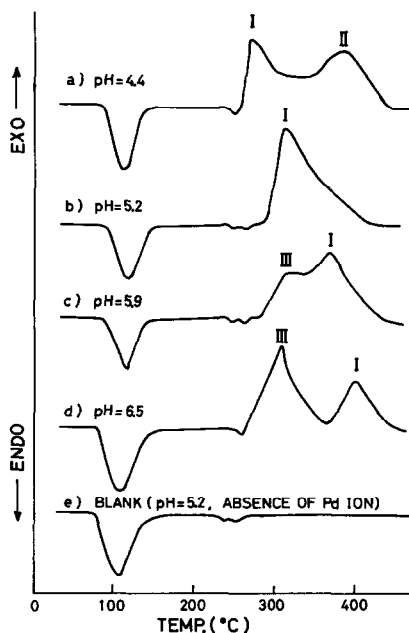


FIG. 13. Differential thermograms of typical ZrP containing Pd cations (Pd content, 0.5 wt%).

cations cannot be discriminated from that due to the change of the cations to PdO. Consequently, the existence of double exothermal peaks in each thermogram observed with other samples (Figs. 13a, c and d and 14d and e) suggests the presence of the Pd cations with the various forms on ZrP. As observed in Fig. 13, the pH increase from 5.2 to 6.5 shifts the peak denoted as I toward higher temperature and another exothermal peak denoted as III appears at a lower temperature. From the tendency of the change in the shift of the peak I, the exothermal peak at a lower temperature in the thermogram of (a) in Fig. 13 should be assigned to the peak I. Figure 14 shows that the increase in the Pd content shifts the single exothermal peak I toward higher temperature. When Pd content exceeded 1.0 wt%, another exothermal peak denoted as IV appeared at a lower temperature with respect to the peak I. The preferred catalyst, prepared at pH 5.2 and containing 0.5 wt% Pd, shows the single peak I (Figs. 13b and 14c). This

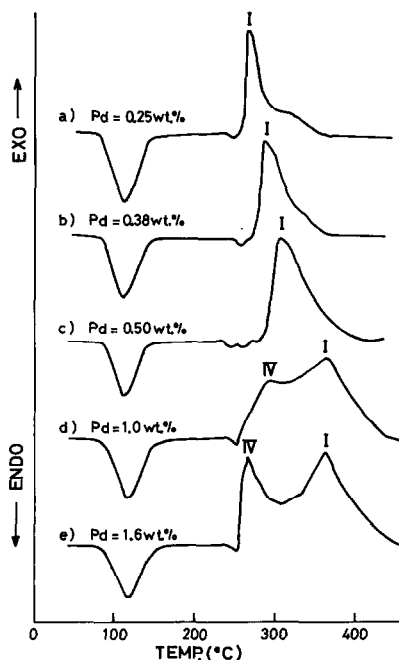


FIG. 14. Effect of the Pd content on thermal change (pH 5.2).

result could be considered to show the close relation between the catalytic activity and the shape of the thermogram.

STRUCTURE AND SELECTIVITY OF THE CATALYST

Crystalline ZrP has been dibasic solid acid $[\text{Zr}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}]$ (11). The titration curve of amorphous ZrP in the hydrogen form does not show two distinct flexion points inherent to a typical dibasic acid (12). However, its acid sites should be dibasic by nature. The appearance of the double exothermal peaks in the thermograms of (c) and (d) in Fig. 13 may be caused by the two types of the distribution of the Pd cations between the strong and weak acid sites of ZrP, because at a pH over 5.9 the Pd cations exist as tetramine-Pd cation as already examined by spectrometry, and also because at such a pH even the weak acid sites of ZrP should be dissociated and combined with the Pd cations. The appearance of the exothermal

peak IV in Fig. 14d and e is probably due to the equilibrated distribution of the ammine-Pd cations between the strong and weak acid sites of ZrP. The double peaks indicated in Fig. 13a suggest the presence of the different kinds of the Pd cations combining with the strong acid sites of ZrP, because both the Pd^{2+} and the ammine-Pd cations are observed at pH 4.3 as indicated in Fig. 8, and because the weak acid sites of ZrP may hardly dissociate in an acidic solution at pH 4.4 and consequently they are incapable of ion-exchanging with any cations. Therefore, low selectivity for the direct synthesis of MIBK should be ascribed either to the introduction of the ammine-Pd cations into the weak acid sites of ZrP by ion exchange (Fig. 15c) or to that of the Pd^{2+} into the strong acid sites (Fig. 15a). Probably, the ammine-Pd cations combining with the weak acid sites cause the appearance of the peak III in Fig. 13 and the peak IV in Fig. 14, and the Pd^{2+} combined with the strong acid sites the peak II in Fig. 13a. By reduction treatment at the higher temperature than 450°C , the Pd cations in these state may be apt to gather to form relatively larger particles of metallic Pd (more than about 40 \AA in diameter) which

promote the formation of isopropyl alcohol.

In contrast, the state of the ammine-Pd cations combining with the strong acid sites of ZrP (Fig. 15b), which corresponds to peak I, causes the formation of the finely dispersed Pd particles (below 30 \AA in diameter), which promote the selective hydrogenation of mesityl oxide to MIBK. Also, the strong acid sites of ZrP are similarly regenerated and the obtained catalyst is useful as a bifunctional catalyst for the direct MIBK synthesis.

In conclusion, the estimated states of the Pd cations combined with ZrP are pictured in Fig. 15.

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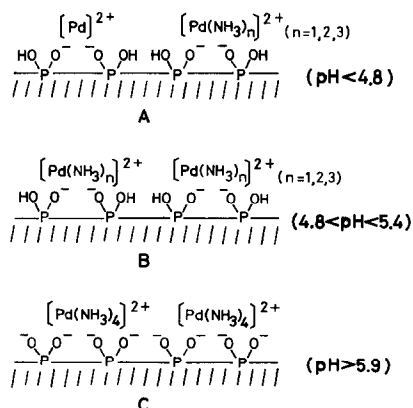


FIG. 15. Estimated state of Pd-ZrP gel: (A) corresponding to (a) in Fig. 13 (less selective); (B) corresponding to (b) in Fig. 13 (selective); (C) corresponding to (c and d) in Fig. 13 (less selective).