Activation of Solid Phosphoric Acid
by Heat Treatment*

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Summary: Solid phosphoric acid is a calcined mixture of kieselguhr and phosphoric acid. The acid components on the finished catalyst surface are ortho-, pyro- and metaphosphoric acids.

As is well known, pyrophosphoric acid is the most active catalyst, while orthophosphoric acid is fairly active and metaphosphoric acid almost inactive. Hence, it may be said that the aim of the heat treatment of the catalyst is to obtain the maximum conversion of orthophosphoric acid into pyrophosphoric acid on the catalyst surface.

The authors observed the change in the acid composition on the catalyst surface in the course of heat treatment with special reference to its influence on the catalytic activity.

The adhered phosphoric acid was successfully extracted from the carrier skeleton without changing its acid composition and analyzed according to the Wazer's pH titration method. The relationship between the catalytic activity and the acid composition of the solid phosphoric acids was fully discussed based on the analytical data of the extracted acid.

The authors also investigated the properties of carrier kieselguhrs. Generally speaking, kieselguhrs having small bulk density and large micropore volume gave excellent catalysts by mild heat treatment. And the stability of their siliceous skeleton to heat and chemicals was found to have an appreciable effect on the activity and mechanical strength of the finished catalysts.

Introduction

Among the acids of phosphorus, pyrophosphoric acid was found, in our early experiments, to be the most excellent catalyst for the olefin polymerization.

The structure observation of phosphoric acids by means of electron diffraction by Dr. S. Yamaguchi1), and the proton exchange mechanism for olefin polymerization proposed by Dr. J. Horiuchi2) supported our experimental results.

The solid phosphoric acid is a calcined mixture of phosphoric acid and some kind of carrier. The starting acid material is orthophosphoric acid and kieselguhr is generally used as the carrier due to its high acid holding power and its acid resisting property.

In this study, the authors observed the change in the acid composition on the catalyst surface in the course of heat treatment with special reference to its influence on the catalytic activity. The authors also investigated the physical properties of various kieselguhrs, such as bulk density, micropore volume and electron microscopic skeleton structure, which may have influence on the effect of heat treatment, and subsequently, on the activity of the finished catalyst.

Heat Treatment of the Solid Phosphoric Acid

The solid phosphoric acid, which is a combination of kieselguhr and phosphoric acid, is generally prepared as following:

Kieselguhr is well mixed with orthophosphoric acid. The wet powder thus produced is dried, pelleted and activated by heat treatment. The conditions of heat treatment are so controlled as to obtain the maximum conversion of orthophosphoric acid into pyrophosphoric acid, which

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is the most active form as polymerization catalyst. When orthophosphoric acid is heated at 200°C, it changes into pyrophosphoric acid gradually. However, it is almost impossible to obtain 100% conversion into pyrophosphoric acid (See Fig. 1 and Fig. 2). When heated at 300°C, the pyrophosphoric acid formation is always accompanied by the metaphosphoric acid formation (See Fig. 3). In the case of the supported phosphoric acid, the heat treatment seems to work more effectively than in the case of the free acid.

In the commercial preparation of the solid phosphoric acid, the muffle furnace has been used so far for the heat treatment of the catalyst. The authors proposed the use of a rotary kiln for the same purpose. By using a laboratory scale rotary kiln, the authors obtained very...
successful results. The laboratory scale rotary kiln with its accessories is shown in Fig. 4.

The activities of the finished catalysts obtained by heat treatment in a muffle furnace are shown in Fig. 5, and those obtained by heat treatment in a rotary kiln in Fig. 6. The activity of each catalyst is represented by the conversion % of propylene, when it is polymerized at 250°C and at a space velocity of 40 under atmospheric pressure in the presence of the catalyst in question4).

**Effects of the Physical Properties of Carrier Kieselguhrs on the Activity of Solid Phosphoric Acid.**

**Electron Microscopic Structure of Kieselguhrs.**

Kieselguhr is composed of the siliceous skeletons of microscopic aquatic plants, know as diatoms, of the class Bacillarieae.

The siliceous skeletons of kieselguhrs are essentially silica (SiO₂·nH₂O). However, they are usually quite different in appearance with each other according to the origin of the diatoms.

According to our former study5) on kieselguhrs as a catalyst carrier, the skeleton structure of kieselguhr primarily controls its physical properties, such as bulk density, adsorbing power, mechanical strength and stability to heat.

Hence, in this study, the authors investigated the minute skeleton structures of kieselguhrs under electron microscope(16).

Three samples of kieselguhrs were used.

(A) Makkari Kieselguhr.
Produced in Makkari, Hokkaido. Deposits of fresh water origin. Mother diatoms are essentially of the class Melosira. The skeleton structure is a hollow cylinder with many small circular holes on the cylinder wall (Fig. 7 (A), Fig. 7 (B)).

(B) Okayama Kieselguhr.
Produced in Okayama Prefecture. Its commercial name is 'Radiolite'. Mother diatoms are of the classes Stephanodiscus and Cyclotella with Coscinodiscus as a minor component. The diatom valves are of the structure of a
thin disc with radially arranged small holes (Fig. 8 (A), Fig. 8 (B)).

(C) American Kieselguhr, Celite.
Marketed by Jons Manville Co., U.S.A. Its commercial name is “Celite”. Mother diatoms are mainly of the class Coscinodiscus. The diatom valves are of the structure of a comparatively large thin disc which is an aggregate of many hexagonal unit cells with a circular hole at the center of each. Easily decomposed to unit cells leaving circular rim fragments behind (Fig. 9 (A), (B)).

The electron micrograph of the above three kieselguhrs are shown in Fig. 7~Fig. 9.

When kieselguhrs are used as a carrier for the solid phosphoric acid catalyst, it is heat treated after impregnated with phosphoric acid. Before the heat treatment, the adhered acid can be completely extracted with cold water from the kieselguhr-phosphoric acid mixtures. However, as the heat treatment proceeds, the extraction becomes more and more difficult. And, when the time of heat treatment is kept constant, the easiness of the extraction depends on the structure of the carrier kieselguhr.

The extraction of the adhered acid from the...
Makkari kieselguhr after heat treatment is most difficult. In other words, the Makkari kieselguhr has the highest acid holding power even after heat treatment.

Fig. 10~Fig. 12 show the electron micrographs of the kieselguhr skeletons of the solid phosphoric acids after heat treatment. The micrographs were taken after removing most of the adhered acid by water extraction. As clearly observed in figures, the Makkari kieselguhr skeleton is most stable to heat treatment even in the presence of phosphoric acid. Hence, it shows high acid holding power after heat treatment. The skeletons of the other two kieselguhrs are not so stable to heat.

As shown later (See Fig. 16~Fig. 20), the Makkari kieselguhr is the most excellent carrier for solid phosphoric acid. This may be partly due to its thermal stability in the presence of the adhered acid.

**Bulk Density and Micropore Volume of Kieselguhrs.**

Bulk density and micropore volume of the kieselguhrs were measured according to the following procedures.

a) Determination of bulk density
About 10 ml of the sample kieselguhr was taken in a graduated cylinder after drying at 110°C. The cylinder was repeatedly dropped from the height of 38 mm for 1500 times by means of an automatic dropping machine. From the settled volume and the weight of the sample, its bulk density was calculated.

b) Micropore volume

Micropore volume was determined according to the method proposed by H.A. Benesi et al. using carbon tetrachloride as an adsorptive.

Fig. 13 shows change in bulk density of the carrier kieselguhrs during the course of heat treatment at 200°C. For removing the adhered acid to 5 gr. of the catalyst, the catalyst was washed 15 times. 1 liter of cold water was used per washing. Bulk density of the residue was measured after drying.

As to the Makkari kieselguhr-base catalysts, bulk density of the water-extracted carrier kieselguhr notably increased with the time of heat treatment. This means, in the case of the Makkari kieselguhr the extraction of the adhered acid becomes difficult as the heat treatment proceeds. In our early experiment, we confirmed the Makkari kieselguhr reacted only slightly with phosphoric acid even at high temperature. Hence, the acid, although strongly adhered to the carrier surface and not extracted with water, is considered not reacting with siliceous skeleton, but still in a catalytically active form.

On the contrary, in the case of the Celite-base catalyst, almost all of the adhered acid was easily removed by water extraction even after heat treatment, and so bulk density of the carrier after extraction remained almost constant during the time of heat treatment.

Among the three kieselguhrs, the Makkari kieselguhr has the smallest bulk density (0.1688) and the highest acid holding power. The Celite has about double the bulk density of Makkari kieselguhr and the lowest acid holding power. The Okayama kieselguhr has about the same bulk density as that of Celite and its acid holding power ranks midway between the two kieselguhrs.

Fig. 14 shows the change in micropore volume of the carrier kieselguhrs in the course of the heat treatment at 200°C. Micropore volume is represented by liquid volume of carbon tetrachloride adsorbed per gram of the catalyst carrier. As in the case of the bulk density measurement, the adhered acid was removed by water extraction prior to the measurement.
original kieselguhr in the early stage of the heat treatment and then gradually increased with heating time.

It was confirmed by the authors that the micropore volume of the original kieselguhr (not impregnated with acid) did not change by heat treatment.

Hence, in the case of Okayama kieselguhr and Celite, the increase of the micropore volume with heating time means the gradual break-up of the kieselguhr skeleton proceeds in the presence of the adhered acid. In the case of Makkari kieselguhr, the kieselguhr skeleton being comparatively stable to heat even in the presence of acid and its acid holding power being high, the micropore volume decrease caused by the remaining acid, after extraction, overcomes the micropore volume increase due to the skeleton break-up in the early stage of the heat treatment. However, in the advanced stage of heat treatment, the break-up of the skeleton becomes active to increase the micropore volume.

These results may be roughly expected from the electron microscopic observation as previously described.

In conclusion, for the preparation of the solid phosphoric acid, the choice of the carrier kieselguhr is of prime importance. The carrier kieselguhr primarily controls the conditions of heat treatment for the activation of the catalyst and often determines the activity of the finished catalyst.

Generally speaking, the kieselguhr having low bulk density, large micropore volume, high acid holding power and high stability to heat even in the presence of the adhered acid is an excellent carrier for the solid phosphoric acid. From this standpoint, the Makkari kieselguhr is the best carrier ever used in our laboratory.

However, starting from some kind of kieselguhr, it is also possible to prepare a catalyst of sufficient activity by proper choice of conditions for its activation.

Relation between the Catalyst Activity and the Form of Phosphoric Acid on the Catalyst Surface

Analyses of Phosphoric Acid Mixture and Extraction of Phosphoric Acid from the Catalyst.

As already mentioned, phosphoric acid in the solid phosphoric acid catalyst is a mixture of ortho-, pyro- and metaphosphoric acid.

Analysis of the phosphoric acid mixture was successfully conducted according to the Wazer’s pH titration method using a pH meter with a sleeve-type calomel electrode. When the sample acid was rich in pyrophosphoric acid, a precipitation analysis was applied in parallel, in which pyrophosphoric acid was precipitated and measured as zinc pyrophosphate.

In the case of our study, the analysis being applied to the extracted acid from the catalyst, it was absolutely necessary to establish an extraction method in which the catalyst acid came into solution without changing its acid composition.

For this purpose, many trials were conducted by using known mixtures of phosphoric acids as samples to observe the stability of the phosphoric acids in acidic or alkaline medium.

One example is shown in Tab. 1 in which a mixture having a composition of 52.17% pyrophosphoric acid and 47.83% orthophosphoric acid was used as a sample. To the eight sample solutions, each containing 0.5000 gr of the sample acid in 100 ml of water, 0 ml, 10 ml, 15 ml, 20 ml, 30 ml, 40 ml and 50 ml of a half normal sodium hydroxide solution was added respectively. Each solution, after alkali addition, was gently boiled for a certain length of time and, after cooling, its acid composition was determined. The time of boiling was varied from 10 minutes to 20, 30 and 60 minutes. Figures in the column of “Pyro Phosphoric Acid %” in Tab. 1 show the percentage of pyrophosphoric acid remaining in the solution after boiling based on the initial input of pyrophosphoric acid. Hence, the figure 100.00 means the total amount of pyrophosphoric acid in the solution remains unchanged.

As clearly observed from Tab. 1, pyrophosphoric acid is quite stable in alkaline medium of pH 11.5 and over. However, in neutral and acidic medium, it changes into orthophosphoric acid. The increase in acidity accelerates this conversion.

Tab. 2 shows the acid acceleration of the pyrophosphoric acid conversion into orthophosphoric acid. To the same sample solution as used in Tab. 1 Experiment, a half normal of hydrochloric acid solution was added. After boiling, the pyrophosphoric acid content was determined by the zinc pyrophosphate precipitation method. In Tab. 2, the consumption of 2.73~2.94 ml of tenth normal sodium hydroxide solution after the precipitation means perfect conversion of pyrophosphoric acid into orthophosphoric acid.

The similar stability tests were applied to the metaphosphoric acid containing samples. Metaphosphoric acid was less stable to acid than
pyrophosphoric acid and easily changed into orthophosphoric acid in acidic medium. However, in the alkaline medium of pH 11.7 and over, the conversion of metaphosphoric acid was negligible.

Based on these experimental data, the authors proposed three extraction methods, which may, if properly applied according to circumstances, be used as efficient tools to observe the acid composition on the catalyst surface.

a) Cold water extraction.

Cold water can extract all the adhered acid from the catalysts before heat treatment. However, from the heat treated catalysts, perfect extraction of the adhered acid is difficult with cold water, especially when the carrier kieselguhr has high acid holding power or some reactivity with acid.

By applying cold water extraction to the heat treated catalysts, we can observe the acid composition of the adhered acid on the outer layer ("the surface acid"), which is most strongly exposed to heat.

In the case of cold water extraction, little change occurs in the acid composition.

b) Hot alkaline extraction.

When the catalyst is treated with the dilute alkaline solution of pH 11.7 and over under boiling, the adhered acid comes into solution, its composition unchanged, even in the case of heat treated catalyst.

c) Hot acidic extraction.

When the catalyst is treated with dilute hydrochloric acid solution under boiling, all the adhered acid comes into solution and is converted into orthophosphoric acid. From this extract, the total amount of the adhered acid can be determined as orthophosphoric acid.

**Relation between the Catalyst Activity and the Form of Phosphoric Acid on the Catalyst Surface.**

As previously mentioned, the catalytic activity of ortho-, pyro- and metaphosphoric acid being very different with each other, it is naturally expected that the acid composition on the

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**Table 1** Pyro-Phosphoric Acid (%) after Hydrolysis in NaOH Solution.

<table>
<thead>
<tr>
<th>pH after Heating</th>
<th>Time of Heating</th>
<th>10 min</th>
<th>20 min</th>
<th>30 min</th>
<th>60 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>49.33</td>
<td>39.47</td>
<td>23.78</td>
<td>10.31</td>
<td></td>
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<tr>
<td>3.0</td>
<td>57.86</td>
<td>45.29</td>
<td>37.22</td>
<td>10.75</td>
<td></td>
</tr>
<tr>
<td>4.5</td>
<td>69.51</td>
<td>60.55</td>
<td>54.27</td>
<td>26.92</td>
<td></td>
</tr>
<tr>
<td>7.0</td>
<td>90.14</td>
<td>88.35</td>
<td>86.10</td>
<td>69.96</td>
<td></td>
</tr>
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</table>

**Table 2** Titration of Pyro-Phosphoric Acid after Hydrolysis in HCl Solution.

<table>
<thead>
<tr>
<th>N/2-HCl ml</th>
<th>Time of Heating</th>
<th>0.5 hr</th>
<th>1 hr</th>
<th>2 hr</th>
<th>4 hr</th>
<th>6 hr</th>
<th>8 hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>11.12</td>
<td>4.82</td>
<td>2.94</td>
<td>2.73</td>
<td>2.94</td>
<td>2.73</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>4.40</td>
<td>2.94</td>
<td>2.73</td>
<td>2.94</td>
<td>2.73</td>
<td>2.94</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>2.94</td>
<td>2.94</td>
<td>2.73</td>
<td>2.94</td>
<td>2.73</td>
<td>2.73</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>2.94</td>
<td>2.73</td>
<td>2.94</td>
<td>2.73</td>
<td>2.94</td>
<td>2.73</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>2.94</td>
<td>2.94</td>
<td>2.73</td>
<td>2.94</td>
<td>2.73</td>
<td>2.73</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>2.73</td>
<td>2.73</td>
<td>2.94</td>
<td>2.73</td>
<td>2.73</td>
<td>2.73</td>
<td></td>
</tr>
</tbody>
</table>
catalyst surface gives much influence on its catalytic activity.

From the analysis of the hot alkaline extract, we can see the mean acid composition of the catalyst acid, and from the analysis of the cold water extract, the outer layer acid composition of the catalyst acid. The latter acid composition is supposed to be more influential on the catalyst activity.

From this standpoint, the relationship between the catalytic activity and the acid composition of the cold water extract of the catalyst acid was observed.

Fig. 15 shows the efficiency of the cold water extraction of the DM/200-series catalysts. The efficiency naturally increased with time of extraction and, at the same time, decreased with time of heat treatment of the catalyst.

Tab. 3 shows the acid composition of the cold water extracts of the DM/200-series catalysts. It is clearly observed in Tab. 3, that heat effect went deeper and deeper to the depth of the adhered acid. Heat being very effectively applied in a rotary kiln, pyrophosphoric acid was a major component of the surface acid only in the case of the slightly heat treated catalyst and metaphosphoric acid formation occurred even in the early stage of heat treatment.

The acid compositions shown in Fig. 16～Fig. 20 are those of the cold water extracts obtained by 30 minutes extraction.

Fig. 16～Fig. 18 show the relationship between the acid compositions of the cold water extracts and the catalytic activity with respect to the DM-, DR- and CC-series catalysts activated at 200°C in a muffle furnace.

For the DM-series catalyst, heat treatment of 4 hours at 200°C in a muffle furnace was enough to obtain a catalyst of high activity. However, heat treatment at 200°C in a muffle

<table>
<thead>
<tr>
<th>Extraction</th>
<th>Cat.</th>
<th>DM/300-0.5</th>
<th>DM/300-1</th>
<th>DM/300-2</th>
<th>DM/300-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 min</td>
<td>Ortho</td>
<td>31.00</td>
<td>37.95</td>
<td>39.93</td>
<td>33.33</td>
</tr>
<tr>
<td></td>
<td>Pyro</td>
<td>60.50</td>
<td>43.04</td>
<td>29.84</td>
<td>27.13</td>
</tr>
<tr>
<td></td>
<td>Meta</td>
<td>8.50</td>
<td>19.01</td>
<td>31.23</td>
<td>39.54</td>
</tr>
<tr>
<td>30 min</td>
<td>Ortho</td>
<td>39.42</td>
<td>37.89</td>
<td>31.33</td>
<td>27.86</td>
</tr>
<tr>
<td></td>
<td>Pyro</td>
<td>46.91</td>
<td>32.06</td>
<td>28.33</td>
<td>35.27</td>
</tr>
<tr>
<td></td>
<td>Meta</td>
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<td>30.05</td>
<td>35.54</td>
<td>36.87</td>
</tr>
<tr>
<td>60 min</td>
<td>Ortho</td>
<td>45.21</td>
<td>33.46</td>
<td>25.01</td>
<td>22.92</td>
</tr>
<tr>
<td></td>
<td>Pyro</td>
<td>44.07</td>
<td>32.26</td>
<td>31.03</td>
<td>30.75</td>
</tr>
<tr>
<td></td>
<td>Meta</td>
<td>10.72</td>
<td>34.28</td>
<td>41.82</td>
<td>46.30</td>
</tr>
<tr>
<td>120 min</td>
<td>Ortho</td>
<td>48.40</td>
<td>34.80</td>
<td>26.61</td>
<td>26.22</td>
</tr>
<tr>
<td></td>
<td>Pyro</td>
<td>41.24</td>
<td>32.89</td>
<td>31.19</td>
<td>32.29</td>
</tr>
<tr>
<td></td>
<td>Meta</td>
<td>10.32</td>
<td>32.31</td>
<td>42.20</td>
<td>41.49</td>
</tr>
</tbody>
</table>
furnace seemed to be too mild for the DR- and CC-series catalysts. In both cases, the rate of formation of pyrophosphoric acid was very slow at 200°C and effective catalysts could not be obtained even by prolonged heat treatment.

Fig. 19 shows the results obtained by heat treatment at 200°C in a rotary kiln. Heat effect was more predominant in a rotary kiln than in a muffle furnace. One hour of heat treatment at 200°C in a rotary kiln was enough for the DM-series catalyst to obtain maximum activity. The DR-series catalyst also showed pretty high activity by the heat treatment of several hours at 200°C, although the heat effect was not so remarkable as in the case of the DM-series catalyst.

Fig. 20 shows the results obtained by heat treatment at 300°C in a rotary kiln with respect to the DR- and CC-series catalysts. The DR-series catalyst showed high activity on
300°C heat treatment in a rotary kiln. However, under the same circumstances, CCₚ catalyst did not show any improvement in activity.

From the general survey of the experimental data shown in Fig. 16〜Fig. 20, it may be said that heat effect on the catalyst acid composition widely varies according to the kind of the carrier kieselguhr even under the same heat treatment conditions, and there exists a certain intimate relation between the catalyst acid composition, especially that of the outer layer of the adhered acid, and the catalytic activity.

Unfortunately we can not tell the catalytic activity numerically based on the catalyst acid composition. We can say only that the general tendency is the increase in the amount of pyrophosphoric acid favors the activity improvement and too much formation of metaphosphoric acid is bad for the catalytic activity, and, at any rate, it is indispensable for preparing a high active catalyst to obtain a high conversion of orthophosphoric acid into pyro- and metaphosphoric acid on the catalyst surface.

The reasons why we cannot establish any numerical relationship between the catalyst acid composition and the catalytic activity may be explained as following:

The catalytic activity may presumably be connected directly with the number of the transferable (or exchangeable) protons on the catalyst surface, which may be supplied chiefly by pyrophosphoric acid and partly by orthophosphoric acid. These active protons may be partly weakened or destroyed by the adhered water film in the early stage of heat treatment and by the metaphosphoric acid film in the advanced stage of heat treatment. These hindering effects on the catalytic activity being "surface phenomena", cannot be numerically estimated only by knowing the composition of the catalyst acid.

**Summary**

1) When orthophosphoric acid is heated at 200°C, it changes into pyrophosphoric acid. When heated at 300°C, the pyrophosphoric acid formation is always accompanied by the metaphosphoric acid formation. In the case of the supported phosphoric acid, the heat treatment seems to work more effectively than in the case of the free acid. Hence, there exist ortho-, pyro- and metaphosphoric acid in the solid phosphoric acid catalyst after the heat treatment.

2) Physical properties of the carrier kieselguhr have a strong influence on the activity of the finished catalyst. Thermal stability in the presence of the adhered acid of some kieselguhrs were observed under the electron microscope and their acid holding power were estimated by cold water extraction. Their bulk density and micropore volume were also measured.

Generally speaking, the kieselguhr having high thermal stability in the presence of the adhered acid, high acid holding power, small bulk density and large micropore volume is the best carrier for preparing solid phosphoric acid of high activity.

In this respect, the authors recommended the Makkari kieselguhr produced in Hokkaido, as the best carrier of solid phosphoric acid.

3) The conditions of the heat treatment must be controlled according to the kind of kieselguhr. A good kieselguhr, such as the Makkari kieselguhr, produces excellent catalyst by mild heat treatment. However, it is also possible to prepare catalyst of fairly high activity starting from the medium grade kieselguhr, such as the Okayama kieselguhr, by controlling the heat treatment conditions.

4) For observing the acid composition on the catalyst surface, three extraction methods of the adhered acid from the catalyst were proposed by the authors. Among these, cold water extraction and alkaline extraction can extract the catalyst acid without changing its composition. The former was used to find the "surface acid" composition and the latter to find the total adhered acid composition.

5) Base on the analytical data of the "sur-
face acid", the relationship between the acid composition and the catalytic activity was discussed.

No numerical relation was found between the two. For this reason, the authors gave an explanation by considering that the catalytic activity has a direct connection with the number of the active protons exposed to the free surface.

**Literature Cited**

2) J. Horiuchi, *ibid*.