Partial Oxidation of Isobutene to Methacrylic Acid on V_2O_5-P_2O_5 Catalysts

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The vapor-phase air oxidation of isobutene was studied with V_2O_5, V_2O_5-TiO_2, V_2O_5-MoO_3, V_2O_5-P_2O_5, V_2O_5-P_2O_5-TeO_2, and heteropoly compound catalysts, such as $H_3PMo_{12}O_{40}$, $Cs_2HPMo_{12}O_{40}$, $H_5PMo_{10}V_2O_{40}$, and $Cs_{2.5}H_{2.5}PMo_{10}V_2O_{40}$, in the presence of water vapor. On pure V_2O_5, the oxidation products were acetic acid and carbon oxides, plus small amounts of acetone and methacrylaldehyde. With the addition of TiO_2 to V_2O_5, the selectivity to acetic acid increased a little, but the formation of methacrylaldehyde disappeared. The addition of MoO_3 to V_2O_5 enhanced the formations of acetone and methacrylaldehyde, to a certain extent, but methacrylic acid was not obtained. With the V_2O_5-P_2O_5 catalysts, the yield of methacrylic acid attained 21 mol%, the sum of the yields of methacrylaldehyde and methacrylic acid attained 30 mol%, and the yield of acetic acid attained also 30 mol%. The P/V atomic ratio=1.6 catalyst was better than the P/V=1.06 catalyst in the formation of methacrylic acid. Further, the performance of the P/V=1.6 catalyst was better than that of the heteropoly compound catalysts. The results were discussed in the light of the acid-base properties of the catalysts.

Methacrylic acid is an important chemical as a raw material of so-called organic glass. It is currently produced by a two-step partial oxidation of isobutene. The first step, oxidation of isobutene to methacrylaldehyde, is performed with multicomponent oxide catalysts which are similar to those used in the oxidation of propylene to acrylaldehyde. A number of studies have been made of this reaction, as summarized in several review articles.[1-4] The second step, oxidation of methacrylaldehyde to methacrylic acid, is performed mostly with heteropoly compound catalysts based on molybdovanadophosphoric acid, $H_{3+x}PMo_{12-x}V_xO_{40}$ (x=1—2), and its salts. Besides the patent information,[2-4] several scientific works have been done on this reaction.[5-10] It is recognized that the effective catalytic performance of heteropoly compounds is ascribed to their eminent acidic property as well as their redox property. However, it is also known that these compounds are decomposed at around 400 °C and lose their catalytic activity.

On the other hand, the V_2O_5-P_2O_5 (P/V=1.0 to 1.2) system is a unique catalyst possessing a surprisingly high selectivity in the oxidation of butane to maleic anhydride and, moreover, it is stable enough at around 400 °C. Recently, it was found that the V_2O_5-P_2O_5 system possesses an enhanced acidic property.[11,12]

In view of the acid-base property of the reactant and product, the enhanced-acid catalyst is expected to be effective for "acid-formation-type" partial oxidations.[13-16] Indeed, the V_2O_5-P_2O_5 catalysts are found to be effective for the oxidation of acrylaldehyde to acrylic acid[17] and that of isobutyric acid to methacrylic acid.[18] Further, it was recently found that propylene is oxidized directly to acrylic acid.[19]

From these findings, we can predict that the V_2O_5-P_2O_5 catalysts are effective for the oxidation of isobutene to methacrylic acid, also. Therefore, in this study, we focused our attention on the oxidation of isobutene to form methacrylic acid, since no detailed information about this reaction has yet been reported.

Experimental

Oxidation Procedures. The reaction was carried out with a continuous-flow system using tertiary butyl alcohol (TBA) as the starting material for isobutene. It was confirmed that almost all of the TBA is converted promptly into isobutene and water over every catalyst tested. The reactor and the experimental procedures were the same as those employed in the previous works.[17-19] Air was fed in from the top of the reactor with a fixed rate of 400 ml (at 20 °C)/min and a mixture of TBA and water with a TBA/H_2O volumetric ratio of 1/4 was introduced into the preheating section of the reactor by means of a micro liquid-feeder. The feed rate was TBA/H_2O/Air=0.014/0.22/1.00 mol h^{-1} and the amount of catalyst used was 10 to 30 g.

The yield (mol%) is defined as (except for carbon oxides); 100·(moles of product)/(moles of TBA fed in). On the assumption that the formation of carbon oxides is accompanied with those of acetone and acetic acid; that is, $C_4H_8 \rightarrow$acetone+CO_x and $C_4H_8 \rightarrow$acetic acid+2 CO_x, the yield of carbon oxides is calculated as follows; 100·([moles of CO_x]−[moles of acetone] −2[moles of acetic acid])/4 (moles of TBA fed in).

Catalysts. The catalysts used in this study were the same as those used in the previous works.[15-19]

Results

Performance of the V_2O_5 Catalyst. The oxidation of isobutene was conducted with a 10 g-portion of pure V_2O_5 catalyst under the conditions described in the Experimental section. The products were acetic acid and carbon oxides, plus small amounts of acetone and methacrylaldehyde. The methacrylic acid was not detected. The change in the yields of the partial oxidation products with the elevation of the reaction temperature is shown in Fig. 1.

Performance of the V_2O_5-TiO_2 Catalyst. The results obtained with a 10 g-portion of the V_2O_5-TiO_2 (Ti/V atomic ratio=6/4) catalyst are shown in Fig. 2. This catalyst was a little more active than the pure V_2O_5 catalyst. The yield of acetone attained 12 mol% at the isobutene conversion of 50 to 70% and selectivity to acetic acid also increased. However, the formation of methacrylaldehyde was not observed.

Performance of the V_2O_5-MoO_3 Catalysts. Figure 3 shows the results obtained with a 10 g-portion of the V_2O_5-MoO_3 (Mo/V=2/8) catalyst. This catalyst was much less active than the pure V_2O_5 catalyst for the consumption of isobutene. A small amount of methacrylaldehyde was obtained, but methacrylic acid was not obtained. The main partial oxidation product was acetic acid. Figure 4 shows the results obtained with a 10 g-portion of the Mo/V=8/2 catalyst. The perfor-

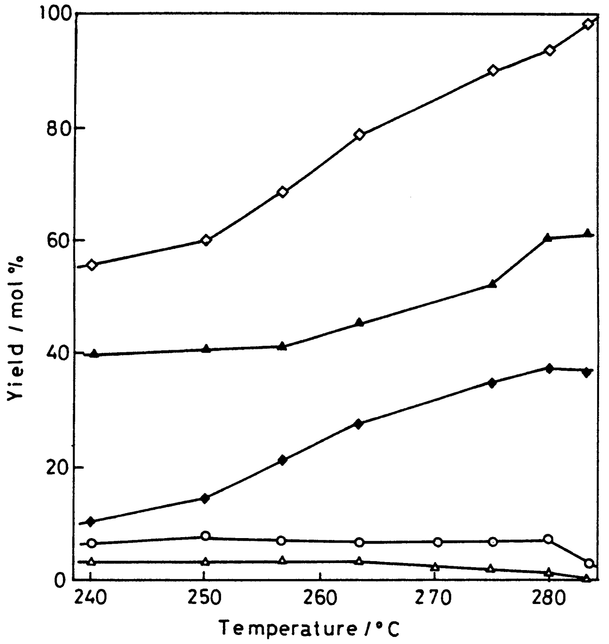


Fig. 1. Oxidation of isobutene with the pure V_2O_5 catalyst. (◇)=isobutene conversion. Yield: (●)=methacrylic acid, (○)=methacrylaldehyde, (▲)=acetic acid, (△)=acetone, (◆)=carbon oxides.

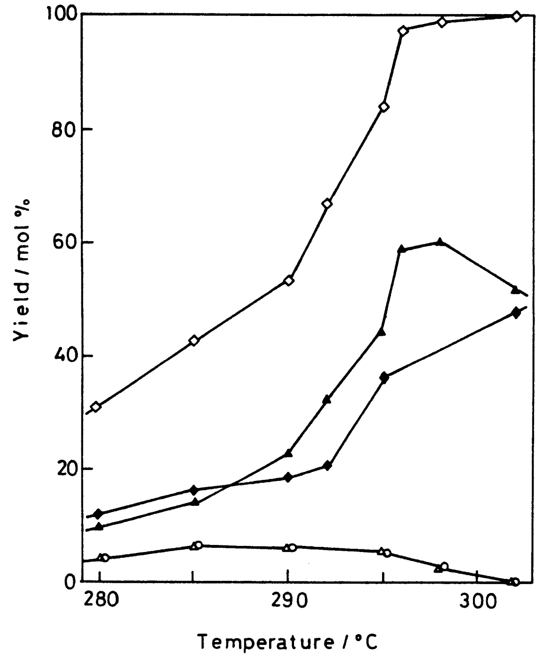


Fig. 3. Oxidation of isobutene with the V_2O_5-MoO_3 (Mo/V=2/8) catalyst. Symbols as in Fig. 1.

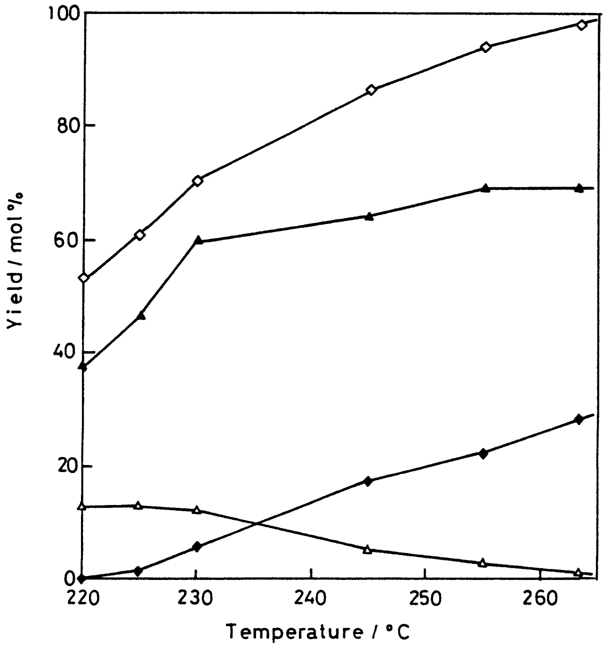


Fig. 2. Oxidation of isobutene with the V_2O_5-TiO_2 (Ti/V=6/4) catalyst. Symbols as in Fig. 1.

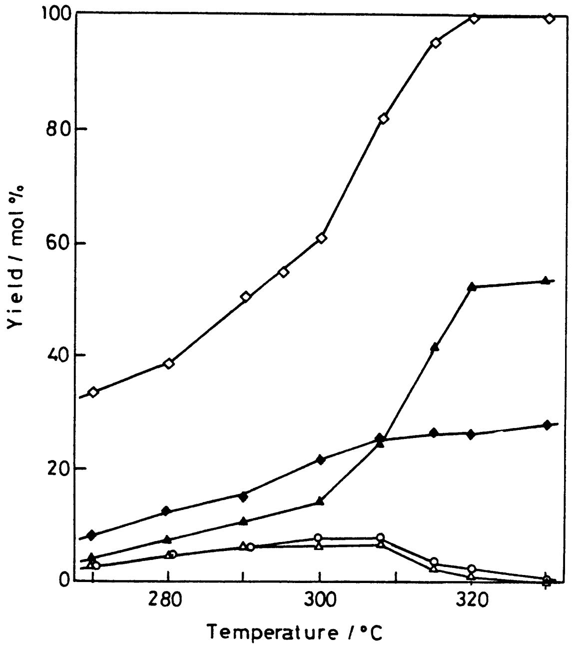


Fig. 4. Oxidation of isobutene with the V_2O_5-MoO_3 (Mo/V=8/2) catalyst. Symbols as in Fig. 1.

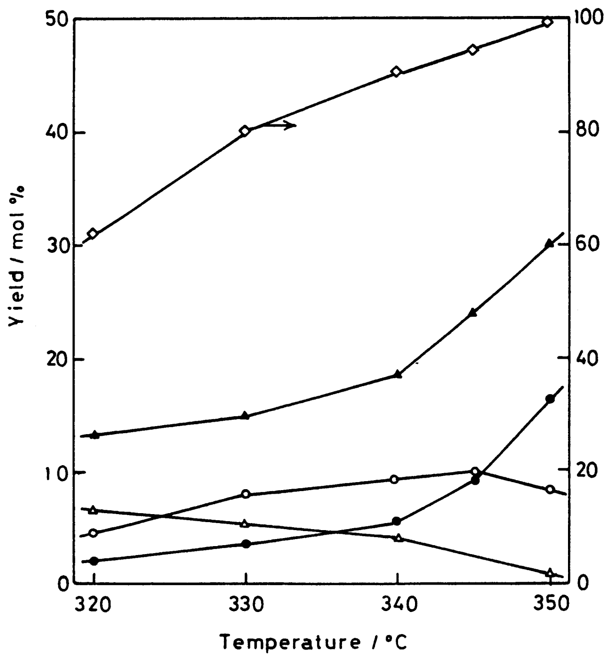


Fig. 5. Oxidation of isobutene with the V_2O_5-P_2O_5 (P/V=1.06) catalyst. Symbols as in Fig. 1.

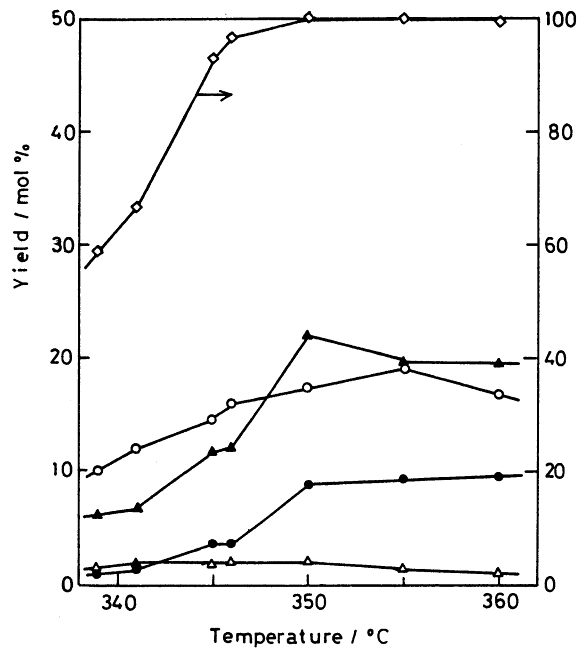


Fig. 7. Oxidation of isobutene with the $H_3PMo_{12}O_{40}$ catalyst. Symbols as in Fig. 1.

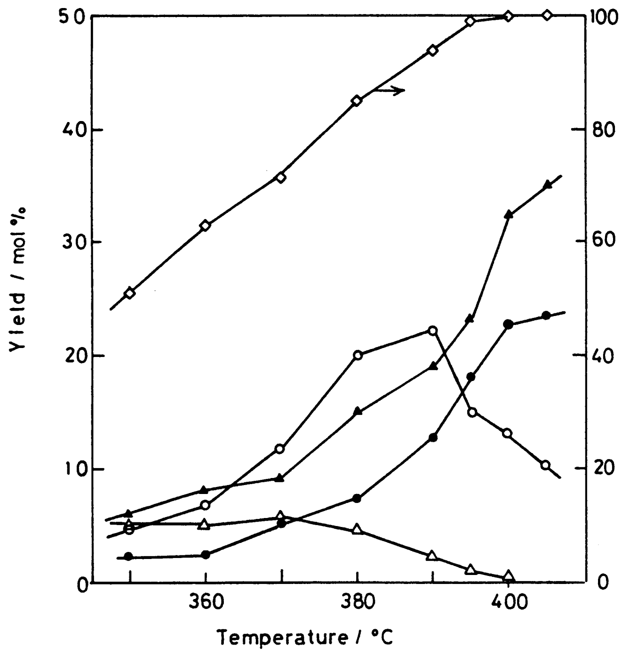


Fig. 6. Oxidation of isobutene with the V_2O_5-P_2O_5 (P/V=1.6) catalyst. Symbols as in Fig. 1.

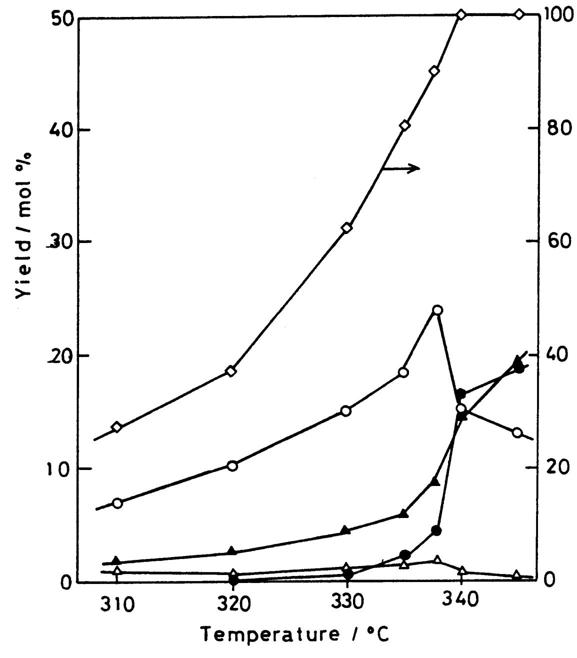


Fig. 8. Oxidation of isobutene with the $Cs_2HPMo_{12}O_{40}$ catalyst. Symbols as in Fig. 1.

mance of this catalyst was similar to that of the Mo/V=2/8 catalyst.

Performance of the V_2O_5-P_2O_5 Catalysts. Figure 5 shows the results obtained with a 20 g-portion of the V_2O_5-P_2O_5 (P/V=1.06) catalyst. The formation of methacrylic acid attained 15 mol% and that of methacrylaldehyde was much greater than in the reaction with the pure V_2O_5 catalyst.

Figure 6 shows the results obtained with a 20 g-portion of the V_2O_5-P_2O_5 (P/V=1.6) catalyst. This catalyst was markedly less active than the P/V=1.06 catalyst. However, the yields of methacrylic acid and methacrylaldehyde were greater. The yield of methacrylic acid attained 21 mol%, the sum of the yields of methacrylic acid and methacrylaldehyde attained about 30 mol%, and the yield of acetic acid attained also about 30 mol%.

Since it has been reported[19] that the V_2O_5-P_2O_5-

TeO_2 ternary system performs better than the V_2O_5-P_2O_5 binary system in the oxidation of propylene to acrylic acid, the Te/P/V=0.15/1.2/1 catalyst was tested in the oxidation of isobutene. It was found that the catalytic performance is not improved by the addition of TeO_2 to the V_2O_5-P_2O_5 system.

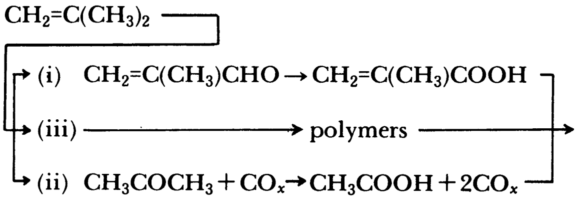
Performance of the Heteropoly Compound Catalysts. Since heteropoly compounds are known to be effective as catalysts for the oxidation of methacrylaldehyde to methacrylic acid, the performance of these catalysts was examined. The results obtained with a 30g-portion of $H_3PMo_{12}O_{40}$ and $Cs_2HPMo_{12}O_{40}$ catalysts are shown in Figs. 7 and 8, respectively. The sum of the yields of methacrylic acid and methacrylaldehyde attained about 30 mol% as in the reaction with the P/V=1.6 catalyst (Fig. 5), but the formation of acetic acid was lower.

The performance of the $H_5PMo_{10}V_2O_{40}$ and $Cs_{2.5}H_{2.5}PMo_{10}V_2O_{40}$ was also tested. It was found that the performances of these catalysts were comparable to that of the P/V=1.6 catalyst.

It should also be noted that the activity of these heteropoly compounds decreases gradually with the duration of the reaction time at temperatures above 350 °C.

Discussion

The character of the curves of methacrylic acid and methacrylaldehyde shown in Figs. 5 and 8 reveals that methacrylaldehyde is an intermediate in the oxidation of isobutene to methacrylic acid. Similarly, the shape of the curves of acetic acid and acetone shown in Figs. 1 to 8 also reveals that acetone is an intermediate in the oxidation of isobutene to acetic acid. Further, it appears that methacrylaldehyde, acetone, and a part of carbon oxides are formed by the following three parallel pathways.



Reaction i is an allylic oxidation, Reaction ii is an oxidative C-C fission, and Reaction iii is a deep oxidation and/or polymerization.

Methacrylaldehyde was not obtained with the V_2O_5-TiO_2 catalyst. This indicates that the catalyst is lacking in the function to promote Reaction i. However, it promotes Reaction ii with a high selectivity than the pure V_2O_5 catalyst. This can easily be understood from the fact that V_2O_5-TiO_2 is very effective as a catalyst for the oxidative C-C fission of butene to form acetic acid.[20,21]

In the case of the pure V_2O_5 and V_2O_5-MoO_3 catalysts, a small amount of methacrylaldehyde was obtained, but methacrylic acid was not obtained. This finding suggests that these catalysts possess a catalytic function to promote Reaction i, to a certain extent, but they are lacking in the function to convert the methacrylaldehyde to methacrylic acid.

Appreciable amounts of methacrylic acid and methacrylaldehyde were obtained with the V_2O_5-P_2O_5 and heteropoly compound catalysts, indicating these catalysts possess both the function to promote Reaction i and that to promote the oxidation of methacrylaldehyde to methacrylic acid. As may be seen in Fig. 5 to 8, the yield of methacrylaldehyde passes through a maximum at the isobutene conversion of about 90%, indicating that methacrylaldehyde is more stable than isobutene under the conditions used.[22]

It has been pointed out[16] that the basic sites of catalyst promote the oxidative C-C fission rather than the allylic oxidation. In line with this thought, the results can be explained as follows. On the pure V_2O_5, about 60 to 70% of isobutene is directed to Reaction ii. The addition of a more basic oxide such as TiO_2 to V_2O_5 enhances the basic property of catalyst.[23] Therefore, the selectivity to Reaction ii increases to about 70 to 90%, but the function to promote Reaction i disappears. On the other hand, the addition of an acidic oxide such as MoO_3 to V_2O_5 induces an increase in the selectivity to Reaction i at the expense of a decrease in the selectivity to Reaction ii. This may be caused by an enhancement of the acidic property and/or a suppression of the basic property.

The addition of P_2O_5 to V_2O_5 induces a marked increase in the acidic property and, at the same time, a marked decrease in the basic property.[11] This may be the reason why a markedly higher selectivity to Reaction i can be obtained with the V_2O_5-P_2O_5 catalysts.

On the other hand, the possession of an enhanced acidic property seems to be required to promote selectively the oxidation of methacrylaldehyde to methacrylic acid.[8] This may be one of the reason why the V_2O_5-P_2O_5 catalysts are effective for the oxidation of isobutene to methacrylic acid.

It has been proposed[15] that heteropoly compounds are similar to V_2O_5-P_2O_5 system in their balance between acidic and basic properties. This may be the reason why similar catalytic performances are obtained in the oxidation of isobutene with the V_2O_5-P_2O_5 and heteropoly compounds.

However, it should be noted that a great extent of Reaction ii is accompanied with Reaction i even with the V_2O_5-P_2O_5 and heteropoly compound catalysts, that is, the suppression of Reaction ii is difficult. This may be a main disadvantage of this process.

It is interesting to note that the P/V=1.6 catalyst exhibits a higher yield of methacrylic acid than the P/V=1.06 catalyst, unlike the case of the oxidation of butane to maleic anhydride, and that the $Cs_2HPMo_{12}O_{40}$ catalyst shows a higher yield of methacrylic acid than the $H_3PMo_{12}O_{40}$ catalyst. At present, it is hard to describe clearly the reason. Further study on the oxidation of methacrylaldehyde is necessary. This will be studied in forthcoming paper.

References

1) D.J. Hucnall, "Selective Oxidation of Hydrocarbons," Academic Press, London/New York, (1974), p. 105.
2) M. Kitahara, *Yuki Gosei Kagaku Kyokai Shi,* **33**, 710 (1975).
3) T. Ohara, *Shokubai (Catalyst),* **19**, 157 (1977).
4) M. Kato, *Shokubai (Catalyst),* **28**, 560 (1986).
5) M. Otake and T. Onoda, *Shokubai (Catalyst),* **18**, 169 (1976).
6) A, G. Perrota, R. B. Bjorklund, J. T. Hoggins, and C. L. Kibby, *J. Catal.,* **61**, 285 (1980).
7) S. Nakamura and H. Ichihashi, Proc. 7th Intern. Congr. Catal., Tokyo, (1981), p. 755.
8) M. Ai, *J. Catal.,* **71**, 88 (1981).
9) M. Ai, *Appl. Catal.,* **4**, 245 (1982).
10) Y. Konishi, K. Sakata, M. Misono, and Y. Yoneda, *J. Catal.,* **77**, 169 (1982).
11) M. Ai, *J. Catal.,* **100**, 336 (1986).
12) G. Busca, G. Centi, F. Trifiró, and V. Lorenzelli, *J. Phys. Chem.,* **90**, 1337 (1986).
13) M. Ai and T. Ikawa, *J. Catal.,* **40**, 203 (1975).
14) M. Ai, Proc. 7th Intern. Congr. Catal., Tokyo, (1981), p. 1060.
15) M. Ai, Proc. 8th Intern. Congr. Catal., Berlin, (1984), V, p. 475.
16) M. Ai, *Polyhedron,* **5**, 103 (1986).
17) M. Ai, *Appl. Catal.,* **27**, 167 (1986).
18) M. Ai, *J. Catal.,* **98**, 401 (1986).
19) M. Ai, *J. Catal.,* **101**, 473 (1986).
20) R. Brockhaus, *Chem. Ind. Tech.,* **38**, 1039 (1966).
21) W. E. Slinkard and P. B. DeGroot, *J. Catal.,* **68**, 423 (1981).
22) J. C. Jungers, "Cinetique Chimique Applique," Technip, Paris, (1958), p. 176.
23) M. Ai, *Bull. Chem. Soc. Jpn.,* **49**, 1328 (1976).