

The Activity of WO₃-based Mixed-Oxide Catalysts

II. Activity and Selectivity in Oxidations of Butene and Butadiene

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The vapor-phase oxidation of 1-butene and butadiene was carried out over a series of WO₃-P₂O₅ catalysts, with different P/W ratios, and over three series of WO₃-P₂O₅-X_nO_m catalysts, with different kinds and amounts of the third component, X_nO_m. Pure WO₃ is fairly inactive, and the introduction of a small amount (P = 1-5 atom%) of P₂O₅ into WO₃ rapidly increases the activity, while the introduction of more than 10 atom% decreases the activity. The activity of the WO₃-P₂O₅ (P/W = 2/8) catalyst increases markedly upon introduction of a small amount (5-10 atom%) of certain third components. The order of this promoting ability is found to be: V₂O₅ > CuO > Cr₂O₃ > MoO₃ > Fe₂O₃. These catalysts show almost the same selectivity to maleic anhydride, whether the reactant is 1-butene or butadiene. The WO₃-P₂O₅-based catalysts are unsuitable for the selective oxidation of butene to butadiene and are inactive for the hydration of butene to an alcoholic intermediate, followed by oxydehydrogenation to form ketone or acetic acid. The catalytic behavior of the WO₃-P₂O₅-based catalysts in the oxidation can be associated with their acid-base properties; that is, they are highly acidic but scarcely basic.

INTRODUCTION

In the preceding paper (1) we reported on the acidic properties of WO₃-P₂O₅ and WO₃-P₂O₅-X_nO_m (X_nO_m = different metal oxides) catalysts and on their correlation with the catalytic activities for the dehydration of isopropyl alcohol (IPA), the isomerization of 1-butene, and the decomposition of cumene.

A variety of mixed-oxide catalysts containing WO₃ have been proposed to be effective for various partial oxidations (2-5), much as in the case of the catalysts containing V₂O₅ and MoO₃. However, the catalytic behavior of the WO₃-based mixed oxides is not as clear as those of the V₂O₅- and MoO₃-based catalysts (2, 3, 6, 7). We have proposed, in previous papers (8-16), that the catalytic behavior of the V₂O₅- and

MoO₃-based mixed oxides in partial oxidations can be interpreted in connection with the acid-base properties of the catalysts.

In this work, we have systematically examined the activity and selectivity of the WO₃-P₂O₅ and WO₃-P₂O₅-X_nO_m catalysts in the oxidations of butadiene and butene in order to clarify the characteristic features of the WO₃-based catalysts and to ascertain how the introduction of some oxides into WO₃ modifies the oxidation activity and how this activity is correlated with the acid-base properties of the catalysts.

EXPERIMENTAL METHODS

The catalysts used in this study were a series of WO₃-P₂O₅ catalysts, with eight different P/W ratios, and three series of

TABLE 1
Catalytic Activity and Selectivity of the WO_3 - P_2O_5
Catalysts for the Oxidation of Butadiene^a

Catalyst atom ratio (W-P)	Activity TC ^b (%)	TC/S ^c (%/m ²)	Selectivity to MA ^d (mole%)
100-0	11	1.8	(9) ^e
99-1	72	9.4	13
98-2	47	6.8	17
95-5	40	6.9	22
90-10	7	2.1	—
85-15	6	2.8	—
80-20	5	2.7	—
70-30	5	2.7	—

^a Butadiene = 0.67 mole% in air; total flow rate = 1.5 liter/min; amount of catalyst = 20 g.

^b Total conversion at 435°C.

^c Total conversion/surface area.

^d Selectivity to maleic anhydride at a conversion of 40-60%.

^e At a conversion of 20%.

WO_3 - P_2O_5 - X_nO_m catalysts (X_nO_m = different kinds of metal oxides), with $X/(W + P + X)$ ratios of 0.05, 0.10, and 0.4 and a constant P/W atomic ratio of 0.2. The WO_3 - P_2O_5 and the $X/(W + P + X) = 0.10$ catalysts were the same as those used in the preceding work, while the others were prepared by the procedures described in the preceding paper (1).

The vapor-phase air oxidations of 1,3-butadiene and 1-butene were carried out in an ordinary continuous-flow reaction system. The reactor and the experimental procedures were the same as those employed in our previous work (8-16). In order to measure the catalytic activity in the stationary state, we usually used data taken more than 2 hr after the start of the experiment.

RESULTS

Since the WO_3 - P_2O_5 -based catalysts are acidic, satisfactory results can be expected merely for the activity in the oxidations of basic reactants and for the selectivity in "base-to-acid"-type reactions (8-16). There-

fore, the oxidations of butadiene and butene were chosen as model reactions.

1. The WO_3 - P_2O_5 System

Butadiene was oxidized in an excess of air ($C_4H_6 = 0.67$ mole%) at 312-470°C over the series of WO_3 - P_2O_5 catalysts. The total flow rate (at 25°C) was kept constant at 1.5 liter/min, and the amount of catalyst used was 20 g. The total conversion of butadiene at 435°C was adopted as a measure of the oxidation activity, for convenience in the experimental procedures; it is shown in Table 1. The selectivity of butadiene to maleic anhydride (MA) at a conversion of about 40-60% was measured for every catalyst; it is also shown in Table 1.

The results indicate that the pure WO_3 is fairly inactive in this oxidation, and that the introduction of a small amount (P = 1-5 atom%) of P_2O_5 into WO_3 rapidly increases the activity, while the introduction of more than 10 atom% of P decreases the activity. The activity does not change in a way very similar to that of the acidity obtained in the preceding work (1). The selectivity to maleic anhydride is not satisfactory compared with that obtained from the MoO_3 - P_2O_5 or V_2O_5 - P_2O_5 catalysts (8, 14).

2. The WO_3 - P_2O_5 - X_nO_m System

In the same way as used before, the total conversion of butadiene and the selectivity to maleic anhydride were obtained for the WO_3 - P_2O_5 - X_nO_m catalysts, with different kinds and amounts of the third component, X_nO_m . The results are listed in Table 2.

The oxidation activity of the WO_3 - P_2O_5 (P/W = 2/8) catalysts, which is fairly low, increases markedly upon introduction of a small amount (5-10 atom%) of certain third components. The order of this promoting ability is found to be: $V_2O_5 > CuO > Cr_2O_3 > MoO_3 > Fe_2O_3$. It is, however, hard to correlate the oxidation activity with the amount of solid acid obtained in

TABLE 2
Catalytic Activity and Selectivity of WO₃-P₂O₅-X_nO_m for Oxidation of Butadiene^a

X	W-P-X (76-19-5)		W-P-X (72-18-10)			W-P-X (50-10-40)		Acidity (<i>r_p</i>) ^e
	Activity (TC) ^b	Sele- ctivity to MA ^d	Activity		Selectivity to MA ^d	Activity		
			TC ^b	TC/S		358°C TC ^c	435°C TC ^b	
V	76	27	(75 × 4)	64	34 ~ 36	65	55 ~ 57	0.06
Mo	(52) ^e	18	56	26	28 ~ 30	42	55 ~ 59	1.0
U			8	1.1	—	14	92	1.3
Ti			23	2.5	17		6	—
Sn			10	4.3	—		26	2
Fe	(48) ^e	30	46	11.5	31	45		10
Al			4	0.6	—		26	5
Bi			15	6.0	—		17	—
Zn			5	0.3	—		9	—
Cr	27	14	78	9.0	12 ~ 16	25		2
Co			19	2.6	5		32	2
Mn			16	4.7	2	13	85	0
Ni			10	1.7	—		36	2
Cu	42	24	80	19.0	28 ~ 31	50		0.5
Mg			14	1.3	9			
K			6	0.4	—			

^a Butadiene = 0.67 mole% in air; total flow rate = 1.5 liter/min; amount of catalyst = 20 g.

^b Total conversion at 435°C; TC/S = total conversion/surface area.

^c Total conversion at 358°C.

^d Selectivity to maleic anhydride (mole percent) at a conversion of 40–60%.

^e Rate of IPA dehydration [*r_p* × 10³ (moles per hour·grams of catalyst)] at 153°C.

the preceding work (1). In the cases of the WO₃-P₂O₅-X_nO_m (W-P-X = 72-18-10) catalysts containing the above-mentioned five oxides, selectivity to maleic anhydride was about 30 mole%, except for Cr₂O₃ (12–16 mole%); in the cases of the other catalysts, which are less active, selectivity is low.

With regard to the W-P-X (50-10-40) catalysts, the catalysts containing the five above-mentioned oxides are also active. The activity of the dehydration for isopropyl alcohol (IPA) was obtained as a measure of the acidity for every catalyst; it is shown in Table 2. No correlation can be obtained between the oxidation activity

and the activity for dehydration (the acidity). A very high selectivity to maleic anhydride (55–59 mole%) is obtained only in the cases of the WO₃-P₂O₅-V₂O₅ and WO₃-P₂O₅-MoO₃ catalysts; for all other catalysts, selectivity was very low, except for WO₃-P₂O₅-Fe₂O₃ which showed a selectivity of 10 mole%.

3. Selectivity of Several Partial Oxidations

In order to obtain more detailed information about the characteristic selectivity of the WO₃-based catalysts, selectivity in several other partial oxidations was examined.

Oxidation of 1-butene to maleic anhydride.

TABLE 3

Selectivity of the $WO_3-P_2O_5-X_nO_m$ Catalysts in the Oxidation of 1-Butene to Maleic Anhydride^a

X	Content of X_nO_m		
	$X/(W + P + X) \times 100$		
	5	10	40
V	28	35	35
Mo	15	30	42
Fe	23	32	—
Cr	10	16	—
Cu	17	31	—

^a Selectivity (mole percent) at a conversion of about 40–60%; 1-butene = 0.67 mole% in air; total flow rate = 1.5 liter/min; amount of catalyst = 20 g; temperature = 350–500°C.

The oxidation of 1-butene was carried out in a manner similar to that used for butadiene over several of the $WO_3-P_2O_5-X_nO_m$ catalysts which show a relatively high selectivity in the oxidation of butadiene to maleic anhydride. The main products were maleic anhydride, CO_2 , iCO , and acetic acid (about one-tenth of maleic anhydride), and the amounts of other

products were not important. The selectivity of butene to maleic anhydride at a total conversion of about 40–60% was measured. The results are shown in Table 3.

It was found that the selectivity to maleic anhydride is almost the same whether the starting material is 1-butene or butadiene, and that the W-P-Mo (50–10–40) catalyst shows a specially high selectivity of 40–43 mole% at a total conversion of 35–80%.

Oxidation of 1-butene to butadiene. Since it was found that, in general, the "acid-formation"-type catalysts are unsuitable for the formation of dienes or aldehydes (8–16), the selectivity of butene to butadiene was examined with the W-P-Cr (72–18–10) and W-P-Fe (72–18–10) catalysts, which are relatively active but which are nonselective for the acid formation. The reaction conditions were: $T = 450^\circ C$; catalyst = 20 g; total flow rate = 1.5 liter/min; 1-butene concentration = 0.67 mole%; oxygen/1-butene = 1/3, and the remainder nitrogen.

It is found that, even in the presence of

TABLE 4

Comparative Data for the Low-Temperature Oxidation of 1-Butene^a

Catalyst (atomic ratio)	Reaction temperature (°C)	Butene conversion (mole%) to				
		MEK	AcOH [$\times (\frac{1}{2})$]	Acetone [$\times (\frac{1}{4})$]	CO + CO ₂ [$\times (\frac{1}{4})$]	Total
W-P-V ^b	280	tr ^c	2.2	tr	1.9	4.1
W-P-Mo ^b	280	tr	1.1	tr	2.2	3.3
W-P-Sn ^b	300	tr	0.0	tr	0.6	0.6
W-P-Cr ^b	300	tr	0.0	tr	0.9	0.9
Sn-V (55–45)	155	0.6	4.7	3.6	0.5	9.4
	190	0.9	8.7	5.8	1.9	17.3
	245	0.5	18.0	6.0	14.8	39.3
Sn-Mo (70–30)	153	11.6	1.4	1.6	0.7	15.3
	170	13.2	2.0	1.8	1.4	18.4
	190	15.3	2.3	1.9	2.1	21.6

^a The flow rates of 1-C₄H₈, air, and H₂O are 10, 60, and 56 ml/min; amount of catalyst = 25 g.

^b W-P-X = 50–10–40.

^c tr, trace amount.

a low concentration of oxygen, the selectivity to butadiene is very low (5–15 mole%, at a total conversion of 20–30%) and that the oxygen is consumed mainly to form CO₂.

Oxidation of 1-butene at low temperature in the presence of water vapor. Another series of butene oxidations was carried out at low temperature (240–300°C) and a low space velocity over several of the WO₃-P₂O₅-X_nO_m catalysts. The flow rates of 1-butene, air, and water vapor were 10, 60, and 56 ml/min, respectively. The amount of catalyst used was 25 g. The results are shown, together with those obtained using the SnO₂-MoO₃ (Mo/Sn = 3/7) and SnO₂-V₂O₅ (V/Sn = 5/5) catalysts (12), in Table 4.

It was found that the WO₃-P₂O₅-X_nO_m catalysts are inactive under these oxidation conditions, and that neither acetic acid nor methyl ethyl ketone can be obtained with these catalysts.

DISCUSSION

In the studies of selective oxidation, many attempts have been made to ascertain the active component in mixed-oxide catalysts and to interpret the catalytic behavior in connection with particular structures (including electronic structures) of the catalysts, as have been reviewed in recent publications (2–5).

However, what are the factors required universally for catalysis in selective oxidations? It has been pointed out as a general rule that the absence of weakly bound oxygen (17–19) or the absence of adsorbed oxygen species (20–23) is a necessary condition for selective oxidations. This condition, however, seems to be far from a sufficient condition. The specific interaction between the catalyst and the reactant must be also taken into account, as commonly thought. Then, what is the general factor deciding this specific interaction?

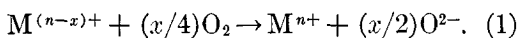
In the previous work, the acid-base properties and their correlation with oxidation activity and selectivity were investigated

for many MoO₃- and V₂O₅-based mixed-oxide catalysts, such as MoO₃-P₂O₅ (8), MoO₃-Bi₂O₃-P₂O₅ (9), MoO₃-V₂O₅ (10), MoO₃-TiO₂ (11), MoO₃-SnO₂ (12), MoO₃-Fe₂O₃ (13), V₂O₅-P₂O₅ (14), V₂O₅-K₂SO₄-H₂SO₄ (15), V₂O₅-TiO₂ (11), V₂O₅-TiO₂-P₂O₅ (16), V₂O₅-SnO₂ (12), and V₂O₅-Fe₂O₃ (13). A generality was established: the catalytic activity for the oxidation of electron-donating (basic) reactants, such as olefinic and aromatic hydrocarbons, is correlated with the acidic nature of the catalyst surface, while catalytic activity for the oxidation of acidic reactants, such as carboxylic acids, is correlated with the basic nature of the catalyst, and selectivity in mild oxidations is governed by the acid-base properties of the catalyst and the reactant.

This evidence led us to the following consideration (24). In the case of mild oxidations, the reactions require the activation of the reactant molecule because the strength of the metal-oxygen bonding is not that weak. Therefore, catalytic activity is decided by the activation of the reactant as well as by the oxidizing power of the catalyst. This reactant activation may be associated with the ease of electron transfer between the catalyst and reactant. In the case of oxidation of electron-donating (basic) compounds, such as olefins, the activation may be ascribed to the acidic sites of the catalyst. On the other hand, in the case of oxidation of acidic compounds, the activation may be ascribed to the basic sites. The difference in the mode or degree of this reactant activation brings about the selectivity of the catalyst.

The oxidizing power of metal oxides may be associated with two factors: (i) the strength of the metal-oxygen bonding (M-O), i.e., the activity of an oxidizing site, and (ii) the possibility of incorporation of gaseous oxygen into the crystal lattice oxygen by electron transfer, i.e., the ability to reoxidize the reduced active sites with gaseous oxygen. It is conceivable

that the reduced metal ions (Lewis base), due to their electron-donating function, give electrons to the gaseous oxygen (acceptor molecule), resulting in the formation of metal ions in a higher oxidation state and lattice oxygen, O^{2-} (Brønsted base):



Therefore, the basic sites which are measured by means of the adsorption of acidic molecules, are supposed to be connected with the surface lattice oxygen, O^{2-} , which can act as the oxidizing site. This leads us to assume that the factor ii is dependent both on (a) the electron-donating ability, i.e., the base strength, of the metal ion in a lower oxidation state, and (b) the number of active lattice oxygen sites, i.e., the basicity. It may be expressed as (24):

Oxidizing power \propto (basicity) ·

$$f(M-O \text{ and base strength}). \quad (2)$$

The proportional relationship between the oxidation activity for hydrogen and the basicity was actually observed in the case of the $MoO_3-Bi_2O_3-P_2O_5$ system (9). We would like to consider, from a general point of view, that the role of a component of lower electronegativity in the catalytic actions of mixed oxides is to strengthen the function of factor ii. The explanations for the role of each component in Cu-Se (25), Fe-As (26), Bi-Mo (27), Sn-Mo (28), Fe-Mo (29), U-Sb (30), and other binary oxide systems (31-33) seem to be based essentially on the same notion as factor ii.

Let us now discuss the experimental results from this point of view. As has been reported in the preceding paper (1), a characteristic of the $WO_3-P_2O_5$ -based mixed-oxide catalysts is a very high acidity, but a very poor basicity; these catalysts are easily reduced by reactant molecules, but the reduced catalysts cannot be reoxidized easily with gaseous oxygen. This evidence leads us to infer that the low oxidation activity of the $WO_3-P_2O_5$ -based catalysts and the absence of a correlation between the oxidation activity for olefins and the

acidity are attributable to their lack of basicity, i.e., that of the above-mentioned factor ii. We assume that, in the case of the $WO_3-P_2O_5$ -based catalysts, oxidation activity is decided by oxidizing power, rather than by activation of the reactant on the acidic sites, unlike the cases of the MoO_3 - and V_2O_5 -based catalysts (8-16).

As $WO_3-P_2O_5$ is strongly acidic, it seems natural that the basic sites of the third components are extinguished. In practice, the high oxidation activity of such oxides as NiO, MnO_2 , and Co_3O_4 , is completely extinguished by combination with $WO_3-P_2O_5$.

However, it is interesting to note that there are several special cases in which the oxidation activity of the third component is not extinguished completely; therefore, the oxidation activity of $WO_3-P_2O_5$ can be enhanced by introduction of these components, though it is too hard at present to understand the reason why. These third components include V_2O_5 , CuO, Cr_2O_3 , MoO_3 , and Fe_2O_3 .

The selectivity of the $WO_3-P_2O_5$ -based catalysts will be discussed next. It has been reported earlier that a requirement for an effective catalyst for a type of partial oxidations such as "basic reactant \rightarrow acidic product" is the acidic property, while that for "basic reactant \rightarrow basic product"-type oxidations, such as the oxidation of butene to butadiene, is a moderate character in both the acid and the base (9-16). As has been expected from the acid-base properties of the $WO_3-P_2O_5$ -based catalysts, a very low selectivity in the oxidation of butene to butadiene and a relatively good selectivity in the oxidation of butadiene to maleic anhydride are obtained in cases in which the catalysts have sufficient activity and the $WO_3-P_2O_5$ is the main component, i.e., $X < 10$ atom%. When the oxidation activity is not sufficient, the reaction, under severe conditions, in our opinion, proceeds nonselectively. However, when the content of the third component is high ($X = 40$ atom%) a good selectivity to maleic anhydride is obtained only when $X = Mo$ and

V. We speculate that the activity of the third component emerges, especially if $X = V, Cu, Cr, Mo,$ and Fe .

It is interesting to note that selectivity to maleic anhydride is almost the same whether the starting reagent is butene or butadiene, and that the WO₃-P₂O₅-based catalysts are inactive in the oxidation of butene at low temperature in the presence of water vapor and have no selectivity for the formation of methyl ethyl ketone or acetic acid under these conditions. On the other hand, with MoO₃-SnO₂ (Mo/Sn = 3/7) and V₂O₅-SnO₂ (V/Sn = 45/55) catalysts, which show a high selectivity to form methyl ethyl ketone and acetic acid, respectively, in the low-temperature oxidation of butene, the selectivity to maleic anhydride from butene (about 20 mole%) is markedly low compared to that from butadiene (about 50 mole%). These results indicate that the main side reaction in the oxidation of butene to maleic anhydride is the hydration of butene to an alcoholic intermediate, followed by the oxydehydrogenation to form ketone (34); in the case of V₂O₅-based catalysts, the produced ketone is easily oxidized to acetic acid (35). The presence of basic sites is required for the oxydehydrogenation of alcohols (8-16). On this basis, it can be well understood why the WO₃-P₂O₅-based catalysts, which are very poor in basicity, are inactive for this side reaction.

It can be concluded that the catalytic behavior of the WO₃-P₂O₅-based mixed oxides in the oxidation is associated with their acid-base properties; that is, they are highly acidic but scarcely basic.

REFERENCES

1. Ai, M., *J. Catal.* **49**, 305 (1977).
2. Margolis, L. Ya., *Advan. Catal.* **14**, 429 (1963).
3. Sampson, R. J., and Shooter, D., "Oxidation and Combustion Reviews" (C. F. H. Tipper, Ed.), Vol. 1, p. 225. Elsevier, Amsterdam, 1965.
4. Villa, P. L., Caputo, G., Sala, F., and Trifirò, F., *J. Catal.* **31**, 200 (1973).
5. Kaneko, K., Hoshino, T., and Wada, S., *Bull. Japan. Petrol. Inst.* **16**, 24 (1974).
6. Voge, H. H., and Adams, C. R., *Advan. Catal.* **17**, 151 (1967).
7. Hucknall, D. J., "Selective Oxidation of Hydrocarbons." Academic Press, London/New York, 1974.
8. Ai, M., and Suzuki, S., *J. Catal.* **30**, 362 (1973).
9. Ai, M., and Ikawa, T., *J. Catal.* **40**, 203 (1975).
10. Ai, M., and Suzuki, S., *Nippon Kagaku Kaishi*, 260, 1973.
11. Ai, M., *Bull. Chem. Soc. Japan* **49**, 1328 (1976).
12. Ai, M., *J. Catal.* **40**, 318, 327 (1975).
13. Ai, M., and Ikawa, T., *Shokubai* **17**, 10 (1975).
14. Ai, M., and Suzuki, S., *Bull. Chem. Soc. Japan* **47**, 3074 (1974).
15. Ai, M., *Bull. Japan. Petrol. Inst.* **18**, 50 (1976).
16. Ai, M., *Bull. Chem. Soc. Japan* **50**, 355 (1977).
17. Sachtler, W. M. H., and de Boer, N. H., "Proceedings, 3rd International Congress on Catalysis, Amsterdam, 1964," Vol. 1, p. 252, 1965.
18. Borekov, G. K., Ven'yaminov, S. A., Sazonova, N. N., Pankrat'ev, Yu. D., and Pitaeva, A. N., *Kinet. Katal.* **16**, 1442 (1975).
19. Pyatnitskii, Yu. I., Golodets, G. I., and Skorbilina, T. G., *Kinet. Katal.* **17**, 148 (1976).
20. Keulks, G. W., *J. Catal.* **19**, 232 (1970).
21. Wragg, R. D., Ashmore, P. G., and Hockey, J. A., *J. Catal.* **22**, 49 (1971).
22. Haber, J., and Grzybowska, B., *J. Catal.* **28**, 489 (1973).
23. Pendleton, P., and Taylor, D., *J. Chem. Soc. Faraday Trans. I*, **72**, 1114 (1976).
24. Ai, M., *Shokubai (Catalyst)* **18**, 17 (1976); *J. Syn. Org. Chem. Japan* **35**, 201 (1977).
25. Kominami, N., Shibata, K., and Minekawa, S., *Kogyo Kagaku Zasshi* **65**, 1510 (1962).
26. Ishikawa, T., and Hayakawa, T., *Kogyo Kagaku Zasshi* **67**, 1931 (1964).
27. Batist, P. A., Lippens, B. C., and Schuit, G. C. A., *J. Catal.* **5**, 55 (1966).
28. Margolis, L. Ya., *J. Catal.* **21**, 93 (1971).
29. Novakova, J., Jiru, P., and Zavadil, V., *J. Catal.* **21**, 143 (1971).
30. Grasselli, R. K., and Suresh, D. D., *J. Catal.* **25**, 273 (1972).
31. Alkhazov, T. G., Belenky, M. S., and Alekseyeva, R. I., Reprints of papers from the 4th International Congress on Catalysis, Moscow, Vol. 1, p. 293, 1968.
32. Niwa, M., and Murakami, Y., *J. Catal.* **26**, 359 (1972).
33. Sala, F., and Trifirò, F., *J. Catal.* **41**, 1 (1976).
34. Buiten, J., *J. Catal.* **10**, 188 (1968).
35. Yamashita, T., Ninagawa, S., and Katoh, T., *Bull. Japan. Petrol. Inst.* **18**, 167 (1976).