JOURNAL OF CATALYSIS **123**, 157–163 (1990)

Surface-Type and Bulk-Type (II) Catalysis in Catalytic Oxidations over 12-Molybdophosphoric Acid and Its Alkali Salts[1]

NORITAKA MIZUNO,[2] TETSUJI WATANABE,[3] HIROO MORI,[4] AND MAKOTO MISONO[2]

Department of Synthetic Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan

Received June 13, 1989; revised December 20, 1989

Several oxidation reactions have been studied over 12-molybdophosphoric acid and its salts in bulk form having different specific surface areas, and in supported form on silica at different loading levels. It has been confirmed experimentally that there are two extreme cases regarding the contribution of processes in catalyst bulk to the overall rate: surface-type and bulk-type (II) catalysis. The rates of bulk-type reactions, such as oxidative dehydrogenation of cyclohexene and oxidation of H_2, changed little with the specific surface area of the unsupported catalysts, while the rates for the supported catalysts increased in proportion to the loading amount up to high loading levels. The results are explained by assuming that diffusion of redox carriers (protons and electrons) is much faster than the rate of overall oxidation. On the other hand, in the case of surface-type reactions such as oxidations of acetaldehyde and CO, the rates were proportional to the specific surface area, and therefore the rates for supported catalysts leveled off at high loadings due to an increase in particle size. The increase was confirmed by narrowing of X-ray diffraction lines. It was presumed that in this case the redox carriers are oxide ions which diffuse relatively slowly.

INTRODUCTION

Catalytic oxidation reactions over mixed oxides often proceed by a redox mechanism (*1–5*). In this mechanism, the reactivity and mobility of the oxide ion often play an important role. Recently, it was reported that heteropoly acid showed high protonic conductivity at room temperature (*6*), and electronic conductivity after partial reduction (*7*). Thus, protons and electrons as well as the lattice oxide ions can be redox or charge carriers in the bulk of heteropoly compounds.

We previously reported that the *stoichiometric* (or noncatalytic) oxidations of various molecules by 12-molybdophosphoric acid and its alkali salts were divided into two groups (*8*). One is the oxidative dehydrogenation reaction, for which the rate per unit weight of catalyst did not depend on the specific surface area. In this case, the reduction of whole catalyst bulk takes place owing to the rapid migration of protons and electrons which are the redox carriers. The other is the oxygen-addition reactions, for which the rate was proportional to the surface area, presumably because the redox carrier is oxide ion and its diffusion is slow. We named the former reactions bulk-type (II) and the latter reactions surface-type (*8, 9*). The former is different from the bulk-type (I) reactions found for acid catalysis at low temperatures. In the bulk-type (I) catalysis, reactant molecules themselves are absorbed in the bulk, where they are transformed into products (cf. Refs. (*9, 10*) for the bulk-type (I) catalysis).

In the present work we mainly investigated how the above differences were reflected in the *catalytic* oxidations of cyclohexene (a bulk-type reactant) and

---

[1] Catalysis by Heteropoly Compounds. XVI.

[2] To whom correspondence should be addressed.

[3] Present address: Central Technical Research Lab., Nippon Oil Co., Ltd., Yokohama 231, Japan.

[4] Present address: Chiba Plant, Asahi Glass Co., Ltd., Ichihara, Chiba 290, Japan.

0021-9517/90 $3.00

acetaldehyde (a surface-type reactant) over supported and unsupported heteropoly compounds. It has already been shown that catalytic oxidations of hydrogen and carbon monoxide follow the same trends as the corresponding stoichiometric reactions (*11*). Heteropoly compounds have attracted attention in the catalytic oxidations of methacrolein (*12*), acrolein (*13*), and methane conversion (*14*). It may be important to recognize the presence of the two types of catalysis, since the two industrial processes for the production of methacrylic acid, i.e., oxidative dehydrogenation of isobutyric acid and oxidation of methacrolein, very likely belong to the two different types (*8*a).

EXPERIMENTAL

Catalysts and reagents. 12-Molybdophosphoric acid ($H_3PMo_{12}O_{40}$, abbreviated as PMo_{12}) was commercially obtained and usually used after purification. Its alkali salts, $M_xH_{3-x}PMo_{12}O_{40}$ (M = Na, Cs, x = 1–3; denoted as M_xPMo_{12}) were carefully prepared as described previously (*8*, *11*). PMo_{12}/SiO_2 catalysts were prepared by incipient-wetness impregnation of SiO_2 (Fuji–Davison), which had been calcined at 500°C for 2 h (300 $m^2 \cdot g^{-1}$ after calcination), with aqueous solution of PMo_{12}. After use in reaction, the catalyst was treated in a N_2 atmosphere and then its surface area was measured again (BET method by N_2 adsorption). Acetaldehyde (Merck–Schuchardt, >99%) was stored in a refrigerator after distillation. Cyclohexene (Tokyo Kasei) was a guaranteed reagent and used without further purification.

Reactions. Catalytic oxidations of H_2 and CO over Na_2PMo_{12} were carried out at 350°C in a closed circulation system (total volume 250 cm^3) as described previously (*11*). In these experiments, the evolved H_2O and CO_2 were condensed in a cold trap. Catalytic oxidations of acetaldehyde and cyclohexene were carried out at 300°C in a flow reactor. The standard procedure was as follows: Catalyst (0.05–0.5 g) was loaded in a reactor and the temperature was raised to 300°C and kept for 1 h in a stream of O_2 (ca. 7 cm^3/min) + N_2 (ca. 63 cm^3/min). Then cyclohexene or acetaldehyde was introduced by passing a part of the stream (N_2 only) through an evaporator saturator. The standard reactant gas compositions were cyclohexene : O_2 : N_2 = 1.2 : 13.0 : 85.8 and acetaldehyde : O_2 : N_2 = 2.3 : 9.6 : 88.1 for the oxidations of cyclohexene and acetaldehyde, respectively. The total flow rates were ca.70 and 30 cm^3/min for the oxidations of acetaldehyde and cyclohexene, respectively, and the carbon balance was usually 85–95% for each reaction.

Analysis. Products of the flow experiments were analyzed by gas chromatography. Products in the gas phase of the outlet were sampled with a stainless-steel sampler kept at 140°C and a microsyringe, for the oxidations of acetaldehyde and cyclohexene, respectively. The GC was equipped with columns containing Porapak Q (for acetaldehyde, acetic acid, methyl acetate, methanol, acetone, and CO_2), molecular sieve 5 Å (for CO), and FFAP (for cyclohexene and benzene).

Other measurements. X-ray diffraction powder patterns were recorded on an X-ray diffractometer (Rigaku Denki, Rotaflex) as described previously (*12*).

RESULTS

Rates of catalytic oxidations of acetaldehyde and cyclohexene over 0.5 g of Na_2PMo_{12} are plotted against the surface area that was measured after the reaction in Fig. 1a. It was confirmed for both reactions that the conversion was proportional to the weight of catalyst at a constant flow rate. In the former reaction, the products were mostly oxygenated products. The selectivity to acetic acid and methyl acetate (*15*) was more than 70% at about 25% conversion level. As seen in Fig. 1a, the rate of acetaldehyde oxidation per weight of catalyst was proportional to the specific surface area. In the latter reaction (cyclohexene dehydrogenation), the selectivity to benzene was above 95%, and the dependency of the rate

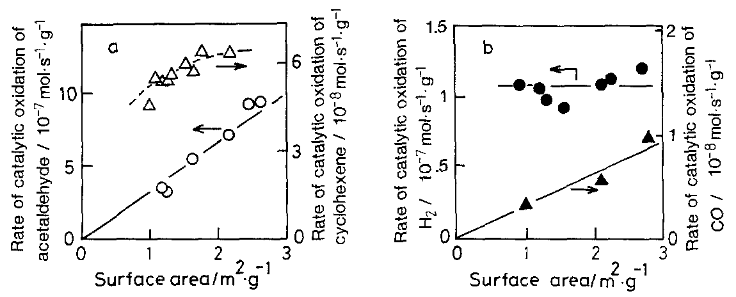

FIG. 1. Rates of catalytic oxidations plotted against specific surface areas of catalyst. Catalyst: $Na_2HPMo_{12}O_{40}$ (8.5 hydrate), 0.5 g. (△) Oxidative dehydrogenation of cyclohexene to benzene at 300°C; (○) oxidation of acetaldehyde to acetic acid at 300°C; (●) oxidation of H_2 at 350°C; (▲) oxidation of CO at 350°C. Some of the data in Fig. 1b have been taken from Ref. (*11*) (10^{-7} mol g^{-1} s^{-1} = 2.4 electron $anion^{-1}$ min^{-1} for Na_2PMo_{12}).

on the specific surface area was much less (Fig. 1a), although it is rather difficult to estimate quantitatively the dependency due to the change in the surface area during the reaction. In Fig. 1b, rates of catalytic oxidation of CO and H_2 over Na_2PMo_{12} are plotted against the surface area, which was measured after the reaction. The surface area decreased by less than 20% during the catalytic oxidation. This figure shows that the rate of catalytic oxidation of CO per weight of catalyst was nearly proportional to the specific surface area, and that the rate of catalytic oxidation of H_2 was almost constant. No structural changes in catalysts were observed by XRD and IR after uses for each catalytic reaction.

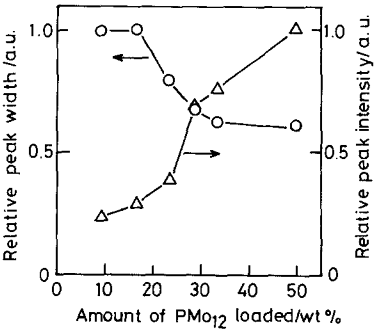

FIG. 2. Relative XRD peak width and intensity of $H_3PMo_{12}O_{40}/SiO_2$ (2θ = 3.3° at the relative peak width = 1.0).

When PMo_{12} was supported on SiO_2 gel, a broad diffraction peak appeared at 2θ = 8.7°, which is characteristic of solid-state PMo_{12}. The XRD peak width and intensity for PMo_{12}/SiO_2 are shown in Fig. 2. A simple mechanical mixture of SiO_2 gel and solid state PMo_{12} (PMo_{12}; 8 wt%) exhibited a sharper and stronger XRD peak than that of corresponding PMo_{12}/SiO_2. As the loading amount of PMo_{12} supported on SiO_2 was increased, the peak width (3.3°) remained unchanged to the loading level of 17 wt%, and then decreased; the corresponding peak intensities increased.

Figure 3 shows the data obtained with different amounts of supported PMo_{12} catalysts. With the increase in the amount of the catalyst, the conversion increased linearly in the oxidations of both acetaldehyde and

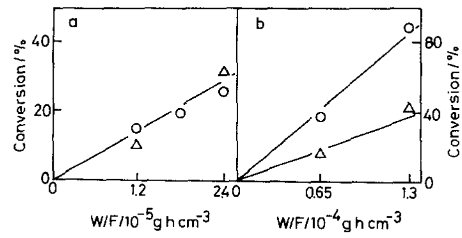

FIG. 3. Rates of catalytic oxidations of acetaldehyde (a) and cyclohexene (b) vs W/F (W, catalyst weight; F, flow rate). Catalysts: $H_3PMo_{12}O_{40}/SiO_2$. Loading amount: (△) 17 wt%; (○) 33 wt%.

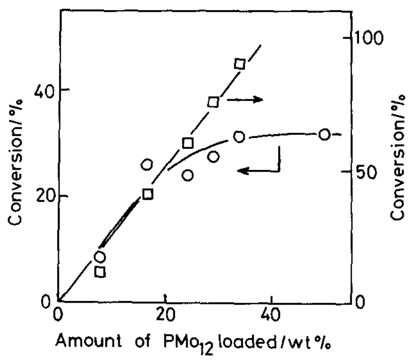

FIG. 4. Catalytic oxidations of cyclohexene (□) and acetaldehyde (○) over $H_3PMo_{12}O_{40}/SiO_2$. Weight of catalysts: 0.2 g for cyclohexene and 0.1 g for acetaldehyde.

cyclohexene (the slope equals the specific activity per mass of catalyst). If one compares the two sets of data ((△) 17 wt% and (○) 33 wt%) in both Figs. 3a and 3b, it is noted that the specific activity increased almost in proportion to the loading amount of PMo_{12} in the dehydrogenation of cyclohexene (Fig. 3b), while the slope changed little with the loading amount in the oxidation of acetaldehyde (Fig. 3a).

In Fig. 4, the conversions of the two oxidation reactions are plotted against the amounts of PMo_{12} loaded on silica gel. In the case of cyclohexene, the conversion increased linearly across the entire range of loadings. In contrast, the conversion of acetaldehyde increased linearly at first, but leveled off at about 20 wt% loading. However, when about 30% water vapor was added in the feed, the oxidation of acetaldehyde also increased linearly with the amount of PMo_{12} until a loading of about 50 wt% was reached.

In Fig. 5, the rates of catalytic oxidation of acetaldehyde and cyclohexene over various salts of 12-molybdophosphates are plotted against the rates of stoichiometric reduction of the catalysts by H_2 or CO. The latter properties are often used to express the oxidation power of catalysts. The following contrast regarding the surface- and bulk-type nature is worthy of note: When the rates of oxidation of acetaldehyde are plotted against the rates of reduction by H_2, little correlation is found (Fig. 5a). In contrast, a good linear correlation is observed between the rates of catalytic oxidation of acetalde-

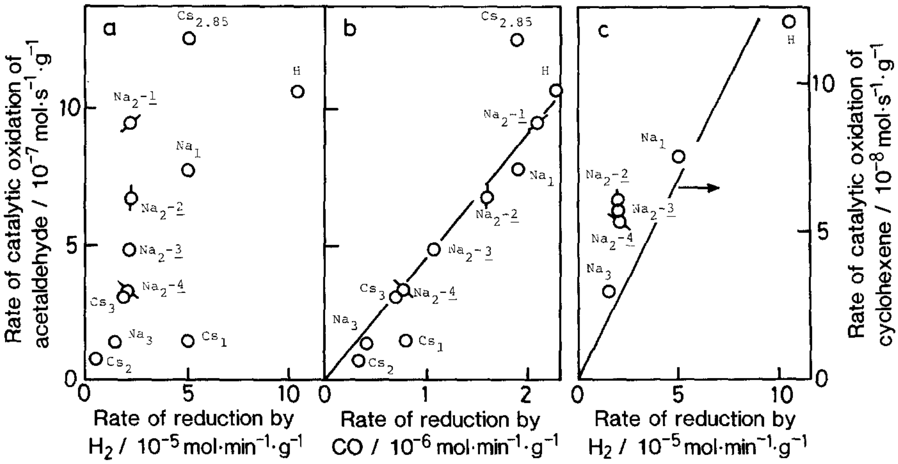

FIG. 5. Correlations between the reducibilities (or the oxidizing abilities) of catalysts and the rates of catalytic oxidations for 12-molybdophosphoric acid and its alkali salts. The reducibilities were measured by stoichiometric reductions by H_2 (bulk-type) and CO (surface-type) (*11*). M_x values denote $M_xH_{3-x}PMo_{12}O_{40}$. Na_2-1, 2, 3, and 4 are $Na_2HPMo_{12}O_{40}$ of different lots. Their surface areas are 2.8, 2.2, 1.7, and 1.2 m^2g^{-1}, respectively.

hyde and those of reduction by CO (Fig. 5b). There is a fair correlation between the rates of oxidation of cyclohexene and those of reduction by H_2 (Fig. 5c).

DISCUSSION

Surface-type vs bulk-type (II) catalysis. We have previously reported that there are two distinct groups in the dependencies of the rate of the reduction of (or *stoichiometric* oxidation by) 12-molybdophosphates on the specific surface area (*8*). To the first group belong reactions in which oxide ions of the polyanion are directly incorporated into the oxidized product (oxygen-addition reactions). Acetaldehyde, methacrolein, and CO are typical reactants. In this group, probably because migration of the oxide ion in the solid bulk of heteropoly acid is relatively slow, the reduction of the polyanions takes place only near the surface. Hence, a linear dependency of the rate on the specific surface area is observed, as in the case of the ordinary solid catalysts.

The second group consists of reactions in which relatively rapid migration of protons and electrons makes possible the reduction of the whole solid. The dehydrogenations of isobutyric acid and cyclohexene and the oxidation of H_2 belong to the second group. With this group, the rate depends little on the specific surface area. We have demonstrated for the case of the stoichiometric oxidation of H_2 by 12-tungstophosphoric acid that the rate changes little with surface area because the rate-determining step is a process in the bulk, that is, the formation of water from protons and polyanion (*16*). In this case, the protons that migrate rapidly between the surface and the bulk are in equilibrium with hydrogen in the gas phase, and the rate was approximately proportional to the partial pressure of hydrogen.

This classification can be directly extended to the *catalytic* oxidations of the reactants examined in the present study. As shown in Fig. 1, the rate of the catalytic oxidations of CO and acetaldehyde were approximately proportional to the specific surface area (or the number of polyanions exposed at the surface) and that rates of the catalytic oxidations of H_2 and cyclohexene were almost independent of the surface area. The dependency of the rate of each reaction on the surface area is exactly the same as that observed previously for the corresponding stoichiometric reaction (*8*). It may be concluded, therefore, that the oxidations of CO and acetaldehyde belong to the surface-type and the reactions of H_2 and cyclohexene belong to the bulk-type.

Thus, there are close correspondences between *stoichiometric* and *catalytic* oxidations regarding the bulk- and surface-type nature. It may be further concluded that two industrially interesting oxidation reactions to produce methacrylic acid over heteropoly compounds, that is, oxidative dehydrogenation of isobutyric acid and oxidation of methacrolein, belong to the bulk- and surface-type, respectively, since these two reactions exhibited the characteristic behavior of each type in the corresponding stoichiometric reactions (*8a*).

The two types of reaction (surface- and bulk-type) may be the two extreme cases. In one case the diffusion of redox carrier is much faster than the overall reaction and in the other case the diffusion was much slower. However, the relative rate of the diffusion to the overall reaction rate may vary depending on the kind of reactions and reaction conditions. Therefore, there must be in general a wide spectrum of reactions between the two extreme cases.

As has been discussed previously for Na_2PMo_{12} (*11*), when the rate of reduction of catalyst by H_2 is independent of the surface area, the rate of the catalytic oxidation of H_2, which proceeds by a redox cycle of the catalyst, depends little on surface area, even though the rate of reoxidation by O_2 is proportional to the surface area. Also, in the case of cyclohexene, the rate of catalytic oxidation depended little on the specific surface area, probably because the rate of the reduction step in the redox cycle did not depend on the specific surface area. The rate of the stoichiometric reduction of Na_xPMo_{12} by cyclohexene was actually little dependent on the surface area (*8*).

The different reaction types are also visible in the results for the supported catalysts, and the effects of loading (Fig. 4) further confirm the presence of bulk-type catalysis as discussed below.

XRD data shown in Fig. 2 demonstrate that, as the loading increased, the particle size of PMo_{12}, which was initially small, started to increase at about a loading level of 17 wt%. The facts that the XRD peak intensity was weak and that the line was broad and changed little below the loading amount of 17 wt% are consistent with the idea that PMo_{12} was dispersed on SiO_2 as fine particles having similar size. The considerable increase in XRD peak intensity and the decrease in peak width above 17 wt% indicate that PMo_{12} particles became large aggregates. Therefore, it is very probable that the outer surface area of PMo_{12} particle (or the number of polyanions exposed to the surface) increased linearly with the loading amount at first, but the increase diminished above ca. 20 wt%. This is consistent with the results reported by Izumi *et al.* (*18*).

Conversion in the catalytic oxidation of acetaldehyde leveled off at a loading of about 20 wt% as shown in Fig. 4. This dependency on the loading is reasonably explained by the change in the particle size as discussed above, since this reaction belongs to the surface-type. If one considers that the particle size is inversely related to the XRD line-width and that there are close correspondences between the data in Figs. 2 and 4, the rate normalized by the number of exposed polyanions would be almost constant for the oxidation of acetaldehyde.

On the other hand, the conversion of cyclohexene increased linearly with loading to a high level. This is also reasonable, because this reaction belongs to the bulk-type category (II), as discussed above for unsupported molybdates. Since the most part of the bulk can take part in the redox cycle, the conversion becomes almost proportional to the weight (or volume) or PMo_{12} present on SiO_2.

The presence of water vapor probably promotes the diffusion of oxide ions in the bulk as water molecules or as hydroxide ions, as was observed previously for stoichiometric reduction by CO (*11*), and would make a surface-type reaction behave more like a bulk-type reaction. Hence, when water vapor was added into the feed, the conversion extended linearly to a higher loading. It is of interest to note that a similar linear correlation up to 60 wt% loading was observed for the oxidation of methacrolein in the presence of water (*12*).

The correlations observed between the rates of oxidation and the oxidizing abilities (Fig. 5) may be understood if one considers the differences in their types of reactions. The oxidizing ability (or reducibility) of catalyst measured by H_2 (a bulk-type reductant for most of the molybdates) reflects the bulk properties and therefore may be used as a measure for bulk-type catalysis (II) like oxidative dehydrogenation of cyclohexene. That measured by CO (a surface-type reductant) corresponds to the surface-type catalysis as observed for oxidation of aldehydes.

In Fig. 6, three types of catalysis found for the catalysis of heteropoly compounds in the solid state are schematically illustrated (taken from Ref. (*19*)). It might be possible that, in addition to the two types discussed above, bulk-type (I) catalysis exists also for oxidation catalysis, in which reactant molecules are transformed to oxidized products

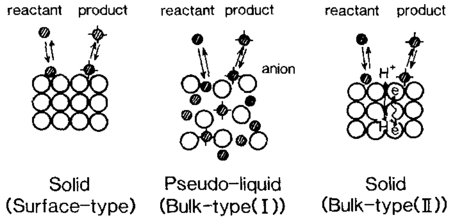

FIG. 6. Schematic illustration of three types of catalysis of heteropoly compounds in the solid state.

in the bulk. However, it has not been found so far.

ACKNOWLEDGMENTS

This study has been supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture (No. 62470070).

REFERENCES

1. Keulks, G. W., *J. Catal.* **19,** 232 (1970).
2. Wragg, R. D., Ashmore, P. G., and Hockey, J. A., *J. Catal.* **22,** 49 (1971).
3. Ueda, W., Moro-oka, Y., and Ikawa, T., *J. Catal.* **70,** 409 (1981).
4. Grasselli, R. K., and Burrington, J. P., *in* "Advances in Catalysis" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 30, p. 133. Academic Press, San Diego, 1981.
5. Sleight, A. W., *in* "Advanced Materials in Catalysis" (J. J. Burton and R. L. Garten, Eds.), p. 181. Academic Press, New York, 1977.
6. Nakamura, O., Kodama, T., Ogino, I., and Miyake, Y., *Chem. Lett.,* 17 (1979).
7. Tamura, Y., Mizuno, N., and Misono, M., in "50th National Meeting, Chem. Soc. Japan, 3F25, Tokyo, 1985."
8. (a) Komaya, T., and Misono, M., *Chem. Lett.*, 1177 (1983); (b) Misono, M., Mizuno, N., and Komaya, T., in "Proceedings, 8th International Congress on Catalysis, Berlin, 1984," Vol. 5, p. 487. Verlag Chemie–Dechema, Frankfurt-am-Main 1984.
9. Misono, M., *Catal. Rev.-Relat. Subj.* **29,** 269 (1987).
10. Misono, M., *in* "Proceedings, Climax 4th Int. Conf. Chemistry and Usage of Molybdenum" (H. F. Barry and P. C. H. Mitchell, Eds.), p. 289. Climax Molybdenum, Ann Arbor, 1982.
11. Mizuno, N., Watanabe, T., and Misono, M., *J. Phys. Chem.* **89,** 80 (1985).
12. Konishi, Y., Sakata, K., Misono, M., and Yoneda, Y., *J. Catal.* **77,** 169 (1982).
13. Serwicka, E. M., Black, J. B., and Goodenough, J. B., *J. Catal.* **106,** 23 (1987).
14. Ahmed, S., and Moffat, J. B., *J. Phys. Chem.* **93,** 2542 (1989).
15. Methyl acetate was confirmed to be formed by acid-catalyzed reaction of $2CH_3COOH \rightarrow CH_3COOCH_3 + CO + H_2O$. Ready CO elimination from carboxylic acid has also been observed in the reaction of isobutyric acid over heteropoly acid (*17*). The details will be discussed in a forthcoming paper.
16. Mizuno, N., and Misono, M., *J. Phys. Chem.* **93,** 3334 (1989).
17. Otake M., and Onoda, T., *J. Catal.* **38,** 494 (1975).
18. Izumi, Y., Hasebe, R., and Urabe, K., *J. Catal.* **84,** 402 (1983).
19. Misono, M., *Mater Chem. Phys.* **17,** 103 (1987); Misono, M., *Stud Surf. Sci. Catal.* **44,** 267 (1988).