Bull. Chem. Soc. Jpn. Vol. 79, No. 1, 145–148 (2006)

Decomposition of Chlorobenzene over Phosphate and Sulfate Catalysts Properties

Yusaku Takita,* Yoshitaka Sadatomi, Hiroyasu Nishiguchi, and Katsutoshi Nagaoka

Department of Applied Chemistry, Faculty of Engineering, University of Oita, Dannoharu, Oita 870-1192

Received June 23, 2004; E-mail: takita@cc.oita-u.ac.jp

The catalytic conversion of chlorobenzene (CB) over some metal phosphates and sulfate was studied in the presence of water vapor and oxygen. The conversion of CB proceeded in the order of $AlPO_4$, $Zr_3(PO_4)_4$, $CePO_4$–$AlPO_4$, and $La_2(SO_3)_3$ above 673 K. The major products were CO, CO_2, and HCl. The reaction proceeded in the absence of water vapor; however, the activity was greatly reduced in the absence of oxygen. Even in the presence of oxygen, 30 mol % of water vapor inhibited the reaction. No intermediate hydration products were observed. There was no correlation between each of the catalytic activity, the acidity, and the concentration of the surface hydroxys of the catalysts. These results suggest that the essential reaction for CB conversion is oxidation. The specific surface area (SSA) of the catalysts was not changed during the CB conversion.

The incineration or oxidation method is actually used for the decomposition of organic compounds containing chlorine.[1] This method requires a high temperature more than 1273 K, and often produces polychlorodibenzoparadioxines (PCDDs) and polychlorodibenzofurans (PCDFs) as by-products, which are well known to be toxic chemicals. These compounds are chemically and microbiologically stable because of the presence of chlorine atoms.

Chlorobenzene (CB) has been used as a model compound for PCDDs. The catalytic decomposition of chlorine-containing compounds is thought to be a superior method compared with the incineration method, because it can be achieved at much lower temperatures. Van den Brink et al. studied the decomposition of CB (500 ppm) in the presence of air and C_7H_{14} (1500 ppm) over 2% Pt/γ-Al_2O_3, and reported that CB completely decomposed to CO_2 at 548 K,[2,3] and CB (1300 ppm in 15% O_2 and 85% N_2) completely decomposed to carbon oxides over MnO_x (3.2 wt %)/TiO_2 at 673 K. These reports show that CB can be completely decomposed using noble-metal catalysts and metal oxide catalysts within the temperature range of 523–673 K.

The authors have studied the decomposition of chlorofluorocarbons (CFCs) using various catalysts and have found that metal phosphates, especially zirconium(IV) and aluminum phosphates, and sulfates are very active in the decomposition of CFCs. These catalysts showed a long life in the presence of strong acids, such as HCl and HF. The essential reaction is hydrolysis, and oxidation proceeds at higher temperatures, via the reaction mechanism via the bidentate surface intermediates and so on.[4–14]

Metal phosphates are potent and very tough catalysts, which are able to work under severe reaction conditions in the presence of strong acids. Since wastes contain various compounds as impurity, environmental catalysts are required to exhibit decomposition activity for many compounds. The catalytic activity of metal phosphates for the decomposition of CB, which has an aromatic ring and a chlorine atom, was studied in the present work.

Experimental

Catalyst Preparation. Zirconium(IV) phosphate and aluminum phosphate catalysts were prepared by the precipitation method described below. An aqueous solution of 10 wt % ammonia was slowly added into an aqueous solution composed of stoichiometric amounts of zirconium(IV) or aluminum nitrate (0.5 M) and 85% *ortho*-phosphoric acid by stirring until the pH of the solution became 4.5. The obtained precipitate was washed well with pure water and filtrated. The resulting powder was pressed into a cylindrical form, crushed, and sieved into 14–32 mesh granules, and was finally calcined at 1000 °C for 5 h in air. The $AlPO_4$ catalyst containing Ce was prepared using a solution containing Ce(III) nitrate together with Al nitrate and phosphoric acid. The catalyst containing Ce was ascertained for a mixture of $CePO_4$ and $AlPO_4$ by an XRD analysis. The catalyst is denoted as $CePO_4$–$AlPO_4$ (Ce/Al = 1/9) in this paper. The specific surface areas of the catalysts before and after the reaction were 106 (103) for $AlPO_4$, 102 (101) for $Zr_3(PO_4)_4$, 30.4 (31.6) for $CePO_4$–$AlPO_4$, and 0.6 (0.5) for $La_2(SO_4)_3$, respectively.

TPD of Water Vapor and Ammonia. The amount of irreversibly adsorbed water vapor was determined by the TPD (temperature programmed desorption) method. The sample was evacuated at 823 K for 1 h, a sufficient amount of water vapor was introduced at the same temperature, and the sample was cooled to 373 K. Next, water vapor on the sample was flushed with a He stream and the TPD was measured in a He flow ($40\,cm^3\,min^{-1}$) at a rate of $10\,°C\,min^{-1}$ after the baseline became stable. Similarly, NH_3 was introduced at 373 K on the catalyst pre-evacuated at 823 K, and then flushed with a He stream.

Reaction Procedure. Catalytic reactions were carried out at atmospheric pressure using a continuous flow reaction system with a fixed catalyst bed reactor, as used by Takita et al.[13] The reaction conditions were as follows. The amount of catalyst used was 4.5 g. Standard feed gas consisted of 1.2–1.8 mol % CB, 17.8 mol % O_2, 10.0 mol % H_2O, and the balance N_2. The feed rate was approximately $41.0\,cm^3\,min^{-1}$. CB was supplied by a saturator (bubbler) maintained at 298 K and O_2 as a carrier gas.

Published on the web January 13, 2006; DOI 10.1246/bcsj.79.145

Water was supplied to an evaporator/mixer, which was located just in front of the catalyst bed, by a micro-liquid pump and mixed with the gases. The effluent gas from the reactor was analyzed by GC. The reaction products were collected separately in a cold trap kept at liquid-nitrogen temperature for 1 h; they were then heated up to room temperature, and dissolved into methanol. The solution was analyzed by Shimadzu GC-8ATP gas chromatographs (thermal conductivity detector, TCD) with two Porapak Q columns (3 mm i.d. × 5 m N_2 carrier and 3 mm i.d. × 5.5 m H_2 carrier), a molecular sieve 13X (4 mm i.d. × 3 m) column, and a JEOL JMS-AMII 150 Mass Spectrometer.

X-ray diffraction patterns (XRD) were obtained by a Rigaku RINT 2500HF system. The specific surface areas of the fresh and used catalysts were determined by the BET method (N_2 adsorption) using a Carlo Erba SORPTY-1750 analyzer.

Results and Discussion

Thermodynamic Consideration of CB Decomposition. As reported in a previous paper, in the decomposition of CCl_2F_2, as being representative of CFCs, the calculations indicated hydrolysis as being much more feasible than oxidation. The hydrolysis actually proceeded as shown below:

$$CCl_2F_2 + 2H_2O \rightarrow CO_2 + 2HF + 2HCl,$$
$$\Delta H_{298} = -148.0\,\text{kJ}, \quad \Delta G_{298} = -224.5\,\text{kJ}, \qquad (1)$$
$$CCl_2F_2 + O_2 \rightarrow CO_2 + F_2 + Cl_2,$$
$$\Delta H_{298} = 98.1\,\text{kJ}, \quad \Delta G_{298} = 58.3\,\text{kJ}. \qquad (2)$$

Therefore, thermodynamic calculations for several reactions of CB were carried out. Selecting of the oxidation technique is quite difficult for CB reactions. It is meaningless to consider the deep oxidation products, because the greater is the number of oxygen atoms incorporated into the products, the more negative are the ΔG_{298} values. The possibility for the formation of chlorophenol can not be ruled out. However, unfortunately no thermodynamic data for chlorophenol was obtained. Thus, the authors tentatively calculated the oxidation for quinone formation: $C_6H_5Cl + O_2 \rightarrow C_6H_4O_2 + HCl$. The calculated ΔG for the reaction is −257 to −263 kJ, which is a large negative value, as expected. No thermodynamic calculations for hydrogen abstraction of CB were possible due to a lack of thermodynamic data. The ΔG change for the hydrolysis of CB is shown in Fig. 1. As can be seen from the figure, the values are close to zero, suggesting that hydrolysis can proceed between the temperature range 200–1000 K. The equilibrium conversion to C_6H_5OH was calculated approximately to be 73% at 298 K, under conditions of 1.8 mol % CB and 10% H_2O.

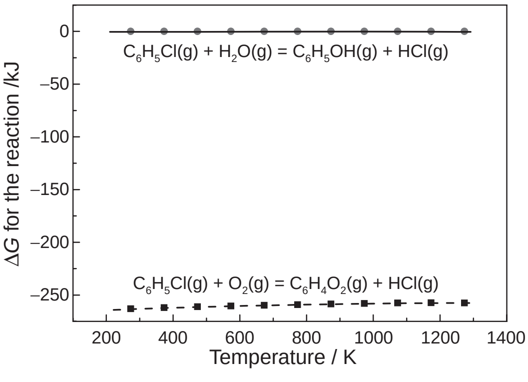

Fig. 1. ΔG changes for hydrolysis and oxidation of chlorobenzene.

Decomposition of CB over Al Phosphates and La Sulfate. The catalytic decomposition of CB was carried out using $Zr_3(PO_4)_4$, $AlPO_4$, Ce-promoted $AlPO_4$, and $La_2(SO_4)_3$ catalysts, which showed very high activity with regard to CCl_2F_2 decomposition.[5,7] The CB conversion and yield of products over various catalysts are shown in Figs. 2 and 3.

The $CePO_4$–$AlPO_4$ catalyst showed the highest activity with regard to the decomposition of CB; CB began to react at 673 K, and the conversion approached 100% at 923 K. The carbon-containing products were CO_2 and CO and no other compounds were observed. Mass analysis of the effluent gas showed no formation of $COCl_2$ and Cl_2. Chloride ions were recovered in a water trap located just after the reactor. Therefore, not $COCl_2$, but HCl, was formed in the reaction. The selectiv-

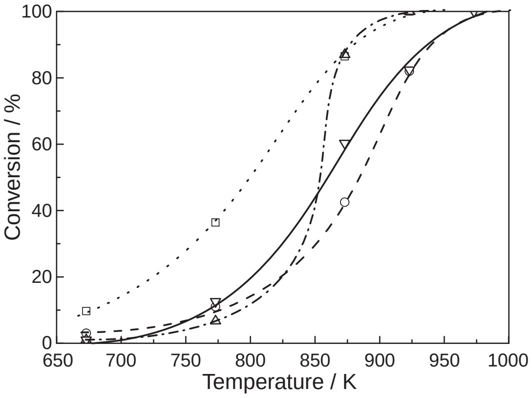

Fig. 2. CB conversion in decomposition over various phosphates and sulfates. Catalyst: 4.50 g; Feed rate ($cm^3\,min^{-1}$): CB 0.54 ($AlPO_4$), 0.60 ($Zr_3(PO_4)_4$), 0.67 ($CePO_4$–$AlPO_4$), 0.71 ($La_2(SO_4)_3$), 7.3 O_2, 29.2 N_2, 4.1 H_2O; ···□···: $CePO_4$–$AlPO_4$ (Ce/Al = 1/9), - -△- -: $Zr_3(PO_4)_4$, —▽—: $La_2(SO_4)_3$, - - -○- - -: $AlPO_4$.

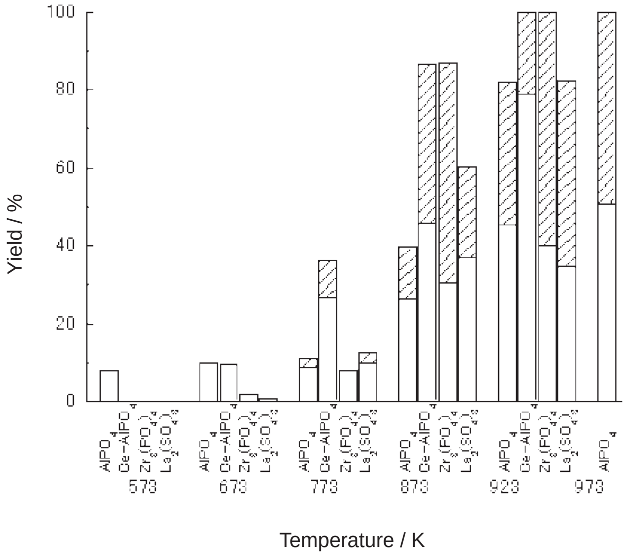

Fig. 3. Yields of the products. ☐: CO_2, ▨: CO. Reaction conditions are the same as those shown in Fig. 2.

ity for CO_2 was 100% when the conversion was below 10%; and the CO_2 selectivity decreased at one instance along with an increase in the temperature, and then increased again.

$Zr_3(PO_4)_4$ registered the next highest activity: The conversion at 773 K was only about 6%; however, it increased sharply and the conversion above 873 K was similar to that of the $CePO_4$–$AlPO_4$ catalyst. $La_2(SO_4)_3$ followed $Zr_3(PO_4)_4$; however, the conversion above 873 K was lower than that of the preceding two catalysts. The activity of $AlPO_4$ was the lowest among these catalysts. The CO_2 selectivity monotonously decreased to 55.3% at 923 K, suggesting that the oxidizing power of the $AlPO_4$ catalyst was lower than that of other catalysts. The order of the catalytic activity of the catalysts was $CePO_4$–$AlPO_4$ > $Zr_3(PO_4)_4$ > $La_2(SO_4)_3$ > $AlPO_4$; and the specific surface areas of the catalysts before and after the reaction were 30.4 and 31.6 ($CePO_4$–$AlPO_4$), 102 and 101 ($Zr_3(PO_4)_4$), 0.6 and 0.5 ($La_2(SO_4)_3$), and 106 and 103 $m^2\,g^{-1}$ ($AlPO_4$). No correlation between the catalytic activity and the SSA of the catalysts was observed. It is significant that the activity of $CePO_4$–$AlPO_4$ was much higher than that of $AlPO_4$, which has the highest SSA. This suggests that the oxidizing power of the Ce-promoted $AlPO_4$ catalyst is higher than that of $AlPO_4$. It is surprising that the $La_2(SO_4)_3$ catalyst, which has only 0.6 $m^2\,g^{-1}$, showed a similar level of activity as the $AlPO_4$ catalyst. The SSAs of the catalysts were measured by N_2 adsorption at liquid-nitrogen temperature; however, the molecular size of CB is larger than that of nitrogen. This means that $AlPO_4$ might have many small pores through which CB could not enter. Since partial oxidation products and phenol were not formed at lower temperatures, the essential reaction under these reaction conditions would be oxidation.

Crystal Structure of the Catalysts. The XRD patterns of the catalysts are shown in Figs. 4 and 5. $AlPO_4$ and $Zr_3(PO_4)_4$ catalysts are amorphous and $AlPO_4$ was partly crystallized. Ce-promoted $AlPO_4$ was well-crystallized and composed of $AlPO_4$ and $CePO_4$. $La_2(SO_4)_3$ was also well-crystallized. The XRD patterns remained unchanged after the reaction, indicating that the catalysts were stable at these reaction conditions.

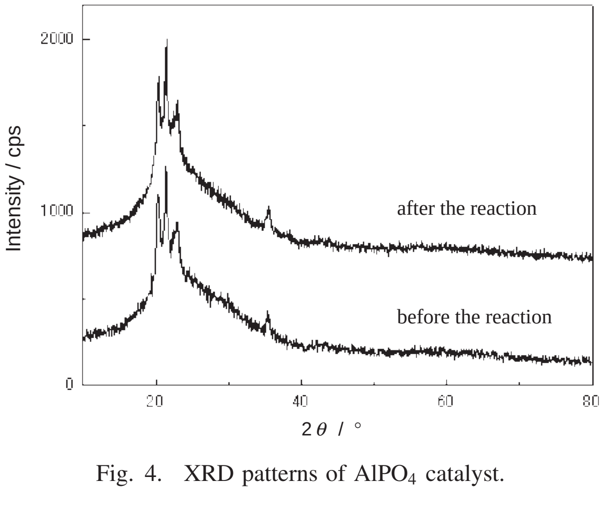

Fig. 4. XRD patterns of $AlPO_4$ catalyst.

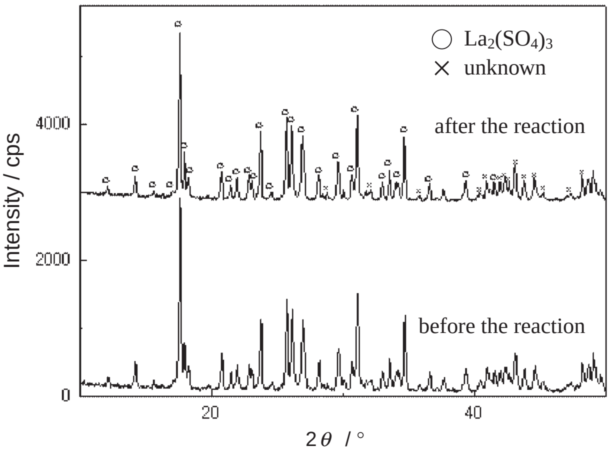

Fig. 5. XRD patterns of $La_2(SO_4)_3$ catalyst.

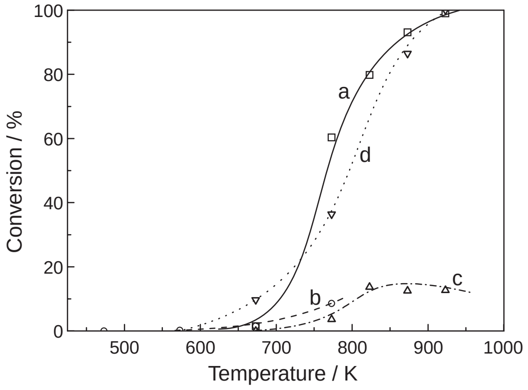

Fig. 6. The effects of O_2 and H_2O concentration on the CB decomposition. Catalyst: $CePO_4$–$AlPO_4$ 4.5 g, Feed concentration (mol %): (a) CB 1.3, O_2 18.0, N_2 80.7, H_2O 0, (b) CB 0.67, O_2 14.1, N_2 55.1, H_2O 30.1, (c) CB 1.36, O_2 0, N_2 88.7, H_2O 10.0, and (d) CB 0.67, O_2 7.3, N_2 29.2, H_2O 4.1.

Effects of O_2 and H_2O on the Decomposition of CB and the Reaction Path. In order to understand the reaction mechanism for CB decomposition, the effects of the concentrations of O_2 and water vapor on the reaction were studied using $CePO_4$–$AlPO_4$; the results are shown in Fig. 6. When no water vapor was introduced in the feed (reaction conditions (a)), the CB conversion was much higher than the results in the presence of 10% water vapor (c). Under the reaction conditions (a), CO_2 was formed at a higher selectivity range 65.9–88.9%, and the rest was CO. When no oxygen was introduced (c), the conversion was as low as 12–13%, even at higher temperatures, such as 823–923 K. No CO was formed, but many partial oxidation products, such as C_2H_5OH, CH_3OH, and C_6H_6, were formed. In particular, C_2H_5OH was formed at 18.6 and 32.3% selectivity at 873 and 923 K, respectively. C_6H_6 was formed at 8.5 and 1.3% selectivity at 873 and 923 K, respectively. However, the formation of phenol, which is the primary product in hydrolysis, was not observed. An explanation of the formation of C_2H_5OH is very difficult, because the fragment compounds from the phenyl group are very small. One hypothesis is that of the formation of C_2H_4 by thermal decomposition at temperatures higher than 773 K, followed by consecutive hydration. However, if this hypothesis is correct, the formation of C_2H_4 should be observed, since the hydration has an equilibrium limitation. Under the condition of a high concentration of water vapor, such as 30 mol % (b), the oxidation of CB was

Table 1. Analysis of Minor Products in the Decomposition of CB[a)]

CB feed rate /μmol min^{-1}	CB conversion /mol %	Rate of formation/μmol min^{-1}			
		CO	CO_2	C_6H_6	$C_6H_4Cl_2$
28.6	7.2	1.9	9.3	tr	0.20

a) Catalyst: $CePO_4$–$AlPO_4$ (Ce/Al = 1/9) 0.9 g, Feed rate (cm^3 min^{-1}): 7.3, N_2 29.2, H_2O 4.1, 773 K.

Table 2. Relation between Catalytic Activity and Physicochemical Properties

Catalyst	Conversion at 873 K/%	SSA/m^2 g^{-1}	Amount of OH /μmol g^{-1}	Acid amount /μmol g^{-1}
$Zr_3(PO_4)_4$	87.0	101	380	67.1
$CePO_4$–$AlPO_4$	86.5	31.6	109	58.1
$AlPO_4$	42.5	103	102	48.6

greatly reduced, and only CO_2 was formed. This may be due to the inhibition of CB adsorption by the competitive adsorption of water vapor. These results support the hypothesis that the essential reaction is oxidation when O_2 and approximately 10 mol % of water vapor are present. The catalysts effective for the decomposition of halogen-containing hydrocarbons require two functions: hydrolysis and oxidation. The decomposition of CFCs requires the function of hydrolysis, rather than oxidation. On the contrary, decomposition of CB requires oxidizing ability than hydrolysis.

Attempt to Detect the Minor Products Formed during the Decomposition of CB. In the case of the oxidation of hydrogen-containing compounds, oxidation of the compounds cannot proceed under water-free conditions, because water is formed by the oxidation of hydrogen-containing compounds. Therefore, all of the reaction products formed at 773 K were collected at liquid-nitrogen temperature for 12 h, and the minor products were carefully analyzed. Under the adopted reaction conditions, the conversion of CB was about 5%. The collected products were warmed to ambient temperature, after which the two solutions, aqueous, and CB solutions, were analyzed by GC-MS, separately. The results are summarized in Table 1. Small amounts of benzene and dichlorobenzene were detected in the CB solution; however, no compounds were formed in the aqueous solution. Benzene and dichlorobenzene can be formed by the disproportionation of CB. It is significant that no trace amount of phenol was formed. These results showed that the decomposition of CB did not occur by hydrolysis, but by oxidation.

Relation between the Catalytic Activity and the Physicochemical Properties. In order to investigate the reaction mechanism, some physicochemical properties of the catalysts were studied, which are summarized in Table 2. The conversion at 873 K was adopted as the index of catalytic activity. No good linear correlation was found among the conversion at 873 K, SSA, the amounts of surface OH, acidic sites of the catalysts. Therefore, it is clear that neither the surface areas nor these physicochemical properties, which are related to the hydrolysis of CB, govern the catalytic activity.

Conclusion

(1) Decomposition of CB proceeded on $AlPO_4$, $Zr_3(PO_4)_4$, Ce-promoted $AlPO_4$, and $La_2(SO_3)_3$ in the presence of oxygen and water vapor above 673 K. CO, CO_2, and HCl were the major products.

(2) The major reaction of decomposition of CB is not hydrolysis, but oxidation.

(3) Phosphate and sulfate catalysts are stable during the decomposition of CB.

References

1 R. Weber, F. Iino, T. Imagawa, M. Takeuchi, T. Sakurai, M. Sadakata, *Chemosphere* **2001**, *44*, 1429.

2 R. W. van den Brink, P. Mulder, R. Louw, *Catal. Today* **1999**, *54*, 101.

3 Y. Liu, M. Luo, Z. Wei, Q. Xin, P. Ying, C. Li, *Appl. Catal., B* **2001**, *29*, 61.

4 G.-L. Li, T. Ishihara, Y. Moro-oka, Y. Takita, *Appl. Catal., B* **1996**, *9*, 239.

5 Y. Takita, G.-L. Li, R. Matsuzaki, H. Wakamatsu, H. Nishiguchi, Y. Moro-oka, T. Ishihara, *Chem. Lett.* **1997**, 13.

6 Y. Takita, T. Ishihara, *Catal. Surv. Jpn.* **1996**, *2*, 165.

7 Y. Takita, M. Ninomiya, R. Matsuzaki, H. Wakamatsu, H. Nishiguchi, T. Ishihara, *Phys. Chem. Chem. Phys.* **1999**, *1*, 2367.

8 Y. Takita, C. Morita, M. Ninomiya, H. Wakamatsu, H. Nishiguchi, T. Ishihara, *Chem. Lett.* **1999**, 417.

9 Y. Takita, M. Ninomiya, H. Miyake, H. Wakamatsu, Y. Yoshinaga, T. Ishihara, *Phys. Chem. Chem. Phys.* **1999**, *1*, 4501.

10 Y. Takita, H. Wakamatsu, M. Tokumaru, H. Nishiguchi, M. Ito, T. Ishihara, *Appl. Catal., A* **2000**, *194–195*, 55.

11 Y. Takita, H. Wakamatsu, G.-L. Li, Y. Moro-oka, H. Nishiguchi, T. Ishihara, *J. Mol. Catal.* **2000**, *155*, 111.

12 Y. Takita, T. Tanabe, M. Ito, M. Ogura, T. Muraya, S. Yasuda, H. Nishiguchi, T. Ishihara, *Ind. Eng. Chem. Res.* **2002**, *41*, 2585.

13 J. Moriyama, H. Nishiguchi, T. Ishihara, Y. Takita, *Ind. Eng. Chem. Res.* **2002**, *41*, 32.

14 Y. Takita, J. Moriyama, H. Nishiguchi, T. Ishihara, F. Hayano, T. Nakajo, *Catal. Today* **2004**, *88*, 103.