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Role of Ti-O-Zr Bonding in TiO_2-ZrO_2 Catalyst for Dehydrogenation of Ethylbenzene

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A relationship between acid amounts over TiO_2-ZrO_2 catalysts and their activities for nonoxidative dehydrogenation of ethyl benzene to styrene was examined. The catalysts were prepared by two different methods; one is simultaneous hydrolysis of Ti and Zr mixed alkoxides solution and the other is physical mixing of pure TiO_2 and ZrO_2. The former consists of fine TiO_2 and ZrO_2 particles and is expected a lot of Ti-O-Zr bonding between the fine particles, while the latter is composed of large particles and less amounts of Ti-O-Zr bonding might be expected. Although the Ti-O-Zr bonding has been considered to generate a new acid site and to enhance the rate of dehydrogenation of ethylbenzene, the acid amounts and the rates observed on unit surface areas of both catalysts were not significantly different. On the basis of these results, the role of Ti-O-Zr bondig in TiO_2-ZrO_2 catalyst for dehydrogenation of ethylbenzene is discussed.

Catalysis by metal oxides often depends upon their surface acidities originated from surface OH groups and structural deficiencies. It has been well-accepted that the surface acidity of a metal oxide can be improved by mixing it with another metal oxide to form a binary oxide.[1] The binary oxide should be prepared by coprecipitation method so as to be composed of fine respective oxide particles, resulting in a lot of metal(1)-O-metal(2) bonding at the fringe of particles. New and strong acid sites generated on the binary oxide have been believed due to the formation of this kind of bonding.[2]

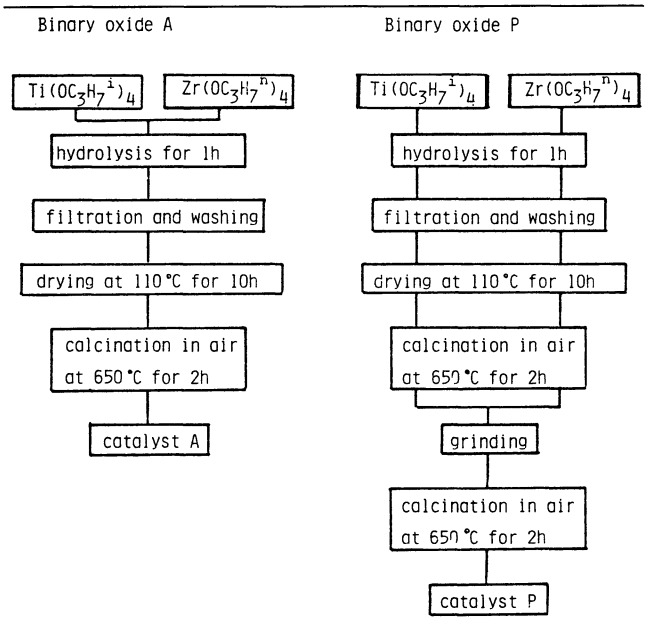
Recently, TiO_2-ZrO_2 binary oxide has been reported to exhibit a high potential for nonoxidative dehydrogenation of ethylbenzene to styrene and this high activity has been explained by a concerted two-center mechanism based on the generation of Ti-O-Zr bonding on the binary oxide catalyst, where Zr ions act as acid sites and Ti as basic sites.[3] Since the catalyst was prepared by coprecipitation of a mixed solution of Ti and Zr tetra chlorides in alcohol with aqueous ammonia, a small amount of chloride ions might remain in the powder as contamination. Considering that the surface acidity is too sensitive to contamination, the catalyst examined should be free from any impurities. In this experiment the TiO_2-ZrO_2 binary catalyst was prepared by simultaneous hydrolytic decomposition of a mixed solution of Ti tetraisopropoxide and Zr tetrapropoxides, which will be one of the best method to prepare oxide powders free from impurities.

The purpose of the present work is to examine the acidity and the rate of dehydrogenation of ethylbenzene on the catalyst thus prepared and to discuss the role of surface Ti-O-Zr bondings during the catalysis.

Experimental

Preparation of TiO_2-ZrO_2 Binary Oxide. The binary oxide composed of TiO_2 and ZrO_2 was prepared by two different methods described in Table 1. In one method, the binary oxide A was prepared by a simultaneous hydrolytic decomposition of titanium tetraisopropoxide (Kishida Chemical Co.) and zirconium tetrapropoxide (Alpha Products Co.) dissolved in benzene. The hydrolysis was carried out at room temperature using an excess amount of distilled water in flowing dry nitrogen. The precipitates thus obtained were dried at 110 °C in an oven, followed by calcination at 500—800 °C in air for 2 h. The weight ratio of TiO_2/ZrO_2 in the binary oxide was varied from 10/90 to 90/10 by changing the amounts of respective alkoxides in an appropriate ratio. In the other method, which will be designated as P, pure TiO_2 and ZrO_2 (total amount being ca. 2 g) were physically mixed and ground in an agate mortar for ca. 30 min, and subse-

Table 1. Preparation Procedures of the Binary Oxides A and P



Preparation procedures of TiO_2-ZrO_2 catalysts.

quently calcined at 650 °C in a similar manner as A. Pure TiO_2 and ZrO_2 were prepared by the hydrolysis of respective alkoxides, followed by drying at 110 °C in an oven and calcination at 650 °C in air. The specific surface areas of these oxides were measured by BET method using nitrogen at its liquid temperature. The structural differences in these binary oxides were studied by X-ray diffraction (Rigaku Denki Co., Geigerflex), operated at 30 kV with a filament current of 15 mA using Ni filter for Cu $K\alpha$ radiation. The distributions of metal ions in the TiO_2-ZrO_2 binary oxide powders were measured by means of EPMA (electron probe X-ray micro analyser, Hitachi Co., X-650), operated at an accelerating voltage of 20 kV. For EPMA measurements the sample powder was covered with thin Pt film to avoid a charge-up phenomenon.

Measurements of Acidity and Catalytic Activity. The surface acidity of the binary oxide was decided by butylamine titration using 1-phenylazo-2-naphthylamine (H_0=+4.0), *p*-dimethylaminoazobenzene (+3.3), benzeneazodiphenylamine (+1.5) and dicinnamal acetone (−3.0), dissolved in benzene, as indicators.[4] The sample powder was first calcined at 650 °C in air and prior to the acidity test the sample was recalcined at 300 °C in O_2 atmosphere, followed by evacuation at the same temperature. The sample thus treated was pored into benzene without exposure to air and a few drops of indicator were added to the sample. The sample was left for 24 h and then submitted to the titration test with butylamine. Several times of the titration tests were made for one sample to decide its surface acidity. The acid amount thus measured has an error larger than +0.1 mmol·g^{-1} because of the difficulty to find out the end point of titration.

The binary oxide powders were employed as catalysts for nonoxidative dehydrogenation of ethylbenzene to styrene. The catalyst powder was calcined at 650 °C for 4 h and the reaction was carried out at 620 °C with a continuous flow reaction system. A mixture of ethylbenzene and water was supplied into the reactor with N_2 stream. The flow rate of N_2 was 25 ml·min^{-1} and the feed rates of ethylbenzene and water were 25 and 43 ml·min^{-1}, respectively. This corresponds to the weight ratio of ethylbenzene/water being 2.

Table 2. Conversions of Ethylbenzene and Selectivities to Styrene, Toluene, and Benzene over the Binary Oxides A and P at 620 °C

Composition (Ti/Zr)	Surface area	EB conversion	Selectivity/%		
	$m^2 g^{-1}$	%	Sty	Tol	Ben
Binary oxide A					
10/90	56	6.7	93.2	2.0	4.8
25/75	92	9.0	94.6	1.7	3.7
50/50	141	11.6	95.5	1.4	3.1
75/25	128	13.6	96.4	1.2	2.4
90/10	113	14.5	96.8	1.1	2.1
Binary oxide P					
10/90	54	7.6	92.4	2.0	5.6
25/75	60	6.5	91.3	2.1	6.6
50/50	40	4.7	91.4	2.7	5.9
75/25	40	6.7	91.0	2.1	6.9
90/10	47	7.1	92.2	3.4	5.8
TiO	50	5.8	92.5	2.4	5.1
ZrO_2	56	3.7	89.0	3.4	7.6

The catalyst powder (2.5 g) was pelleted and placed over the catalyst bed located just below the preheater, containing rashig rings. A cooling trap was equipped at the outlet of the reactor to collect ethylbenzene, water and liquid products such as styrene, benzene and toluene. These liquids were analysed by gas chromatography using a column packed with SP-1200 and Bentone 34 coated Chromosorb W.

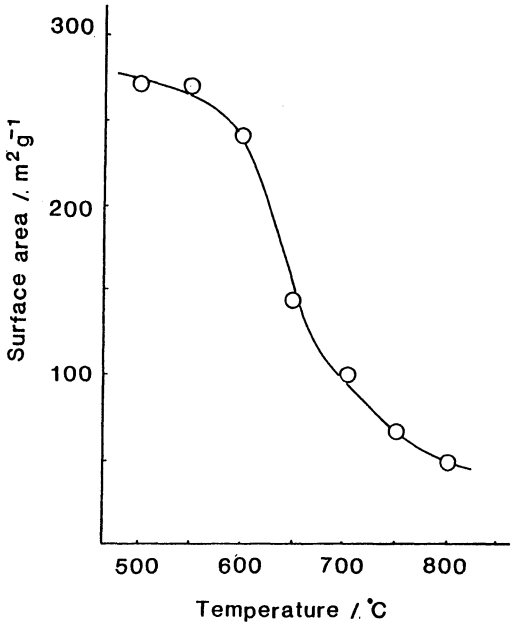


Fig. 1. Change in the surface area of binary oxide A (TiO_2/ZrO_2=50/50) with the calcination temperature.

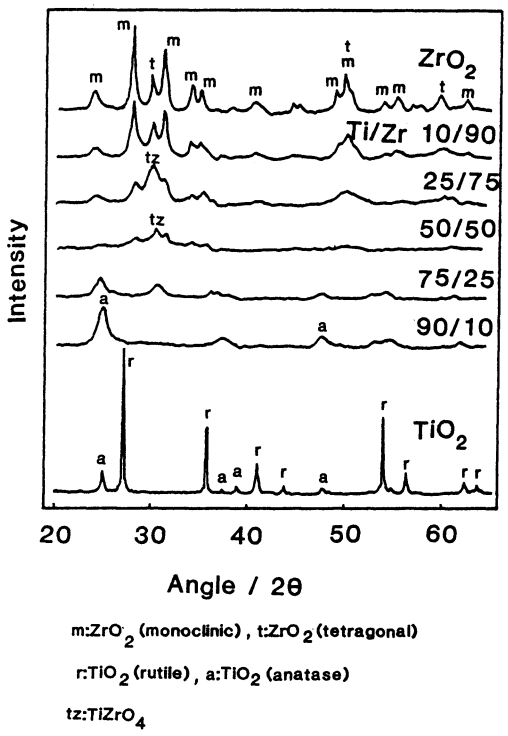


Fig. 2. X-Ray diffraction spectra of the binary oxides A with various TiO_2/ZrO_2 ratios.

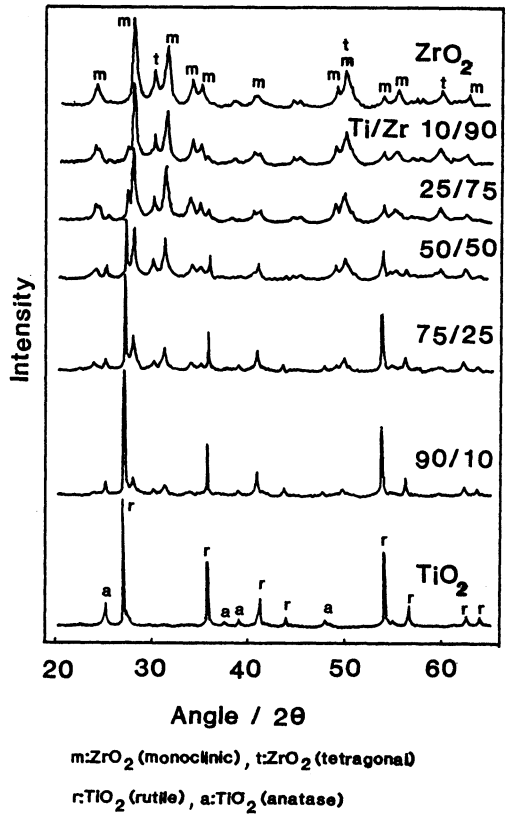


Fig. 3. X-Ray diffraction spectra of the binary oxides P with various TiO_2/ZrO_2 ratios.

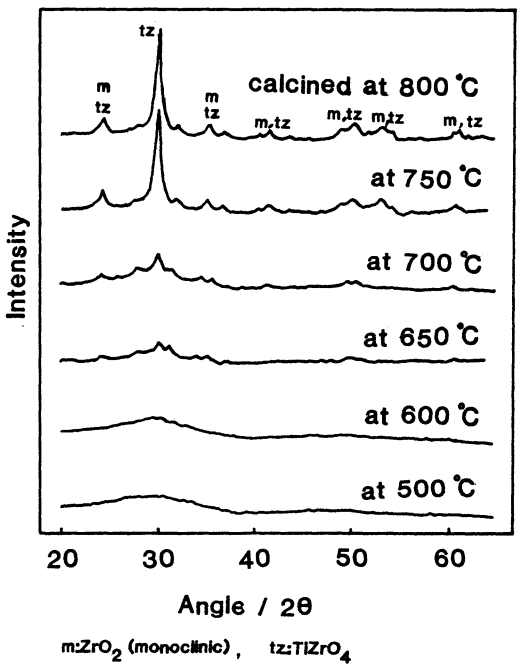


Fig. 4. Change in the X-ray diffraction spectrum of binary oxide A (TiO_2/ZrO_2=50/50) with calcination temperature.

Results

BET Surface Area and X-Ray Diffraction. The BET surface areas of TiO_2, ZrO_2, and the binary oxide powders calcined at 650 °C are listed in Table 2 with other results. The surface area of the binary oxide A (TiO_2/ZrO_2=50/50) decreased with increasing the calcination temperature and reached constant above 750 °C (Fig. 1). The X-ray diffraction spectra of pure TiO_2 and ZrO_2 and the binary oxides are depicted in Figs. 2 and 3. The crystallographic structures of TiO_2 and ZrO_2 are determined to be rutile and monoclinic with a small amount of tetragonal, respectively, when calcined at 650 °C. The binary oxide P calcined at 650 °C showed sharp diffraction peaks assigned to TiO_2 (rutile) and ZrO_2 (monoclinic and tetragonal) with rational intensities according to the respective concentration. On the other hand the binary oxide A calcined at 650 °C showed rather broad diffraction peaks assigned to TiO_2 (anatase), ZrO_2 (monoclinic and tetragonal) and probably to the complex oxide, $TiZrO_4$, when the TiO_2/ZrO_2 ratio of the oxide A is in the range between 25/75 and 75/25. In Fig. 4 are shown the changes in X-ray diffraction pattern of the oxide A (TiO_2/ZrO_2=50/50) with the calcination temperature, indicating that a small amount of $TiZrO_4$ seems to be formed at 650 °C. In the case of binary oxide P, no formation of $TiZrO_4$ was observed even when the powder was calcined at 1100 °C in air for 12 h.

EPMA Measurements. The homogeneous distributions of Ti and Zr ions on the surface of the binary oxide A calcined at 650 °C are demonstrated by X-ray images with EPMA measurements (Fig. 5). While on the surface of the binary oxide P calcined at 650 °C, Ti and Zr ions were found to be localized, forming relatively large TiO_2 and ZrO_2 particles (also in Fig. 5).

Acidity and Catalytic Activity. The total acid amounts on TiO_2, ZrO_2 and the binary oxides calcined at 650 °C were measured by butylamine titration using 1-phenylazo-2-naphthylamine (H_0=+4.0) as an indicator and the results obtained are given in Figs. 6a and b. In Fig. 6a, the acid amount was expressed in terms of $mmol \cdot g^{-1}$, while in Fig. 6b in terms of $\mu mol \cdot m^{-2}$. The strong acid sites with $H_0 \leq +3.3$ were observed on the binary oxide A, while those strong acid sites were never observed on the binary oxide P. The acid amounts with various strengths measured on the binary oxide A are depicted in Fig. 7.

The catalytic activities of TiO_2, ZrO_2, and the binary oxide A and P for dehydrogenation of ethylbenzene at the stationary state are listed in Table 2 and depicted in Figs. 8a and b, where the activities were expressed in terms of $molecules \cdot g^{-1} \cdot s^{-1}$ and $molecules \cdot m^{-2} \cdot s^{-1}$, respectively, assuming first order reaction with respect to ethylbenzene.

Dscussion

The initial stage of the preparation of the binary

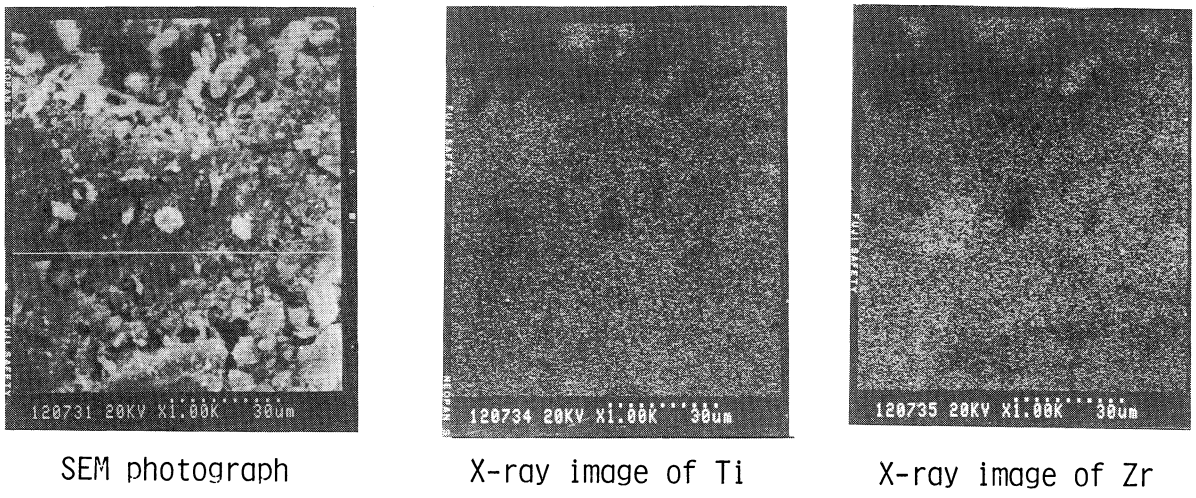


Fig. 5a. Distributions of Ti and Zr ions in the binary oxide A (TiO_2/ZrO_2=50/50) calcined at 650°C, measured by EPMA.

oxide A is the simultaneous hydrolytic decomposition of Ti and Zr alkoxides. Before the hydrolysis, the alkoxides solution was vigorously stirred at 60 °C for 2 h in flowing dry N_2, expecting that the rearrangements of metal ions will take place according to the following reaction;

$$n\ Ti(OC_3H_7)_4 + n\ Zr(OC_3H_7)_4 \longrightarrow [Ti(OC_3H_7)_m\text{-}O\text{-}Zr(OC_3H_7)_m] \quad (1)$$

By adding water the $(OC_3H_7)_m$ groups in the species above were substituted with $(OH)_m$ groups producing propyl alcohol, C_3H_7OH, due to the following reaction;

$$[Ti(OC_3H_7)_m\text{-}O\text{-}Zr(OC_3H_7)_m] + 2m\ H_2O \longrightarrow [Ti(OH)_m\text{-}O\text{-}Zr(OH)_m] + 2m\ C_3H_7OH \quad (2)$$

The hydrogen bonding between (OH) groups in the $[Ti(OH)_m\text{-}O\text{-}Zr(OH)_m]$ species might result in the formation of a gel-like precipitate, where Ti and Zr ions are highly dispersed forming a chemical bonding of Ti-O-Zr. This idea has been already adopted for the preparation of glassy materials such as SiO_2-ZrO_2[5] and SiO_2-TiO_2-ZrO_2[6] systems and of oxide powders such as $BaTiO_3$[7] and $SrTiO_3$.[8] Although the atomic dispersions of Ti and Zr ions are desired, considerable amounts of $[Ti(OC_3H_7)_m\text{-}O\text{-}Ti(OC_3H_7)_m]$ and $[Zr(OC_3H_7)_m\text{-}O\text{-}Zr(OC_3H_7)_m]$ species may be formed in spite of vigorous stirring of the alkoxides solution, and Ti-O-Ti and Zr-O-Zr bondings may also remain in the precipitate produced by hydrolysis. The Ti-O-Ti and Zr-O-Zr structures thus prepared may turn out to be fine TiO_2 and ZrO_2 crystallites, respectively, when the precipitate was dried and calcined in air.

In order to examine the structures of the products, X-ray diffraction patterns of the binary oxide A with various TiO_2/ZrO_2 ratios were obtained (see Figs. 2

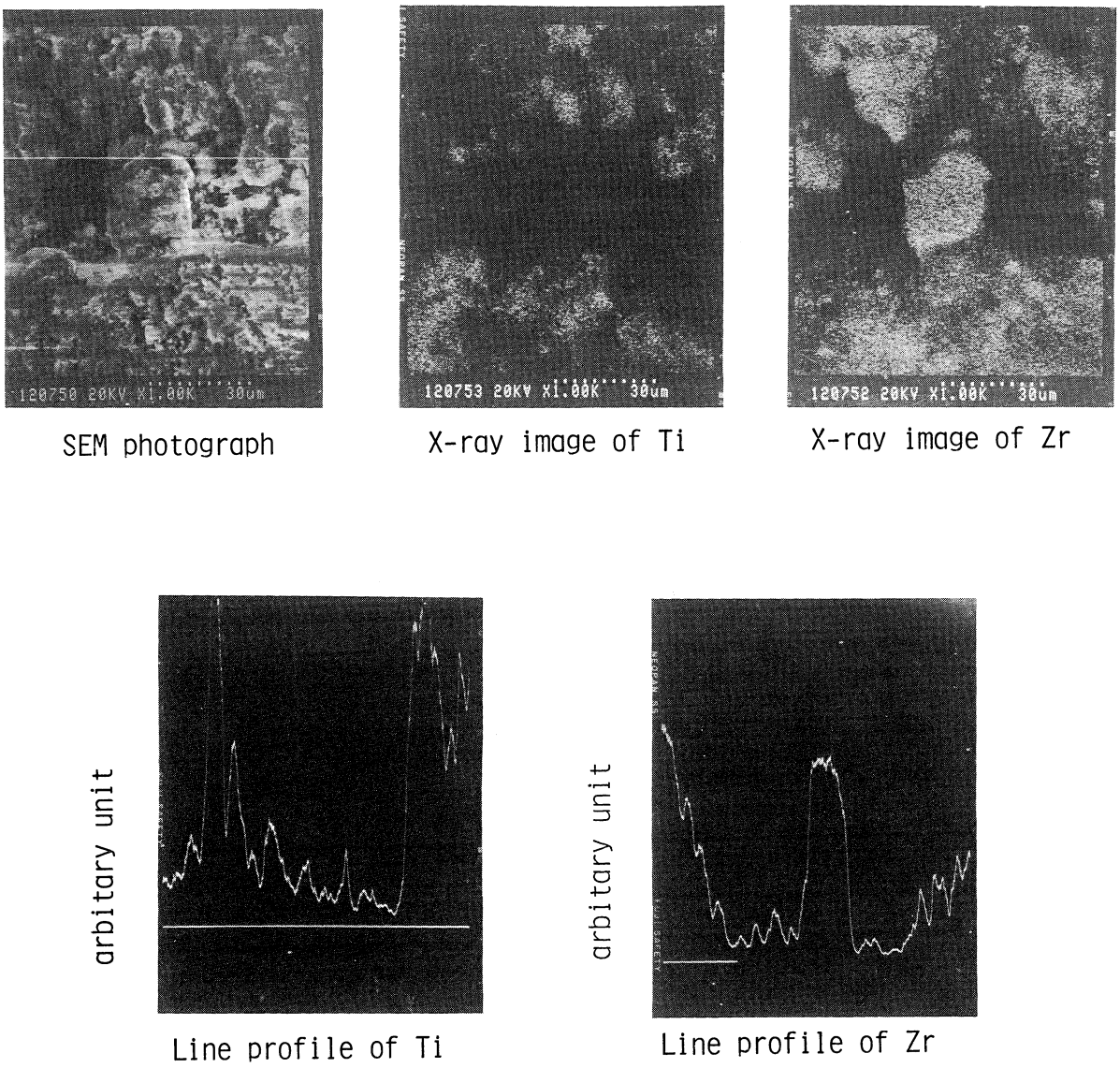


Fig. 5b. Distributions of Ti and Zr ions in the binary oxide P (TiO_2/ZrO_2=50/50) calcined at 650°C, measured by EPMA.

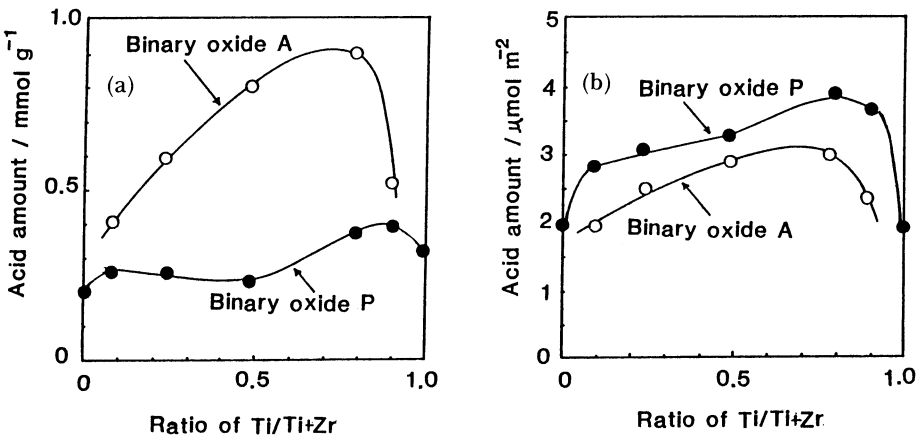


Fig. 6. a) Acid amounts on the binary oxides A and P with varaious TiO_2/ZrO_2 ratios expressed in terms of $mmol \cdot g^{-1}$; the oxides were calcined at 650°C. b) Acid amounts on the binary oxides A and P with various TiO_2/ZrO_2 ratios expressed in terms of $\mu mol \cdot m^{-2}$; the oxides were calcined at 650°C.

and 3). Several broad peaks were observed for the binary oxide A calcined at 650 °C with TiO_2/ZrO_2 ranging from 25/75, while for pure TiO_2 and ZrO_2 sharp diffraction peaks assigned to rutile and monoclinic with a small amount of tetragonal form, respectively, were observed. This indicates that the coexistence of Ti and Zr ions in the precipitate prevents the fine TiO_2 and ZrO_2 crystallites from their crystalline growth during calcination. It might be possible to say that the suppressions of the crystalline growth are attributed to formation of Ti-O-Zr network structure. As could be seen in Fig. 4, the formation of a small amount of $TiZrO_4$ was first observed when the binary oxide A was calcined at 650 °C for 4 h, which resulted in the reduction of the surface area of the oxide A (see Fig. 1). On the contrary, no peaks assigned to $TiZrO_4$ were observed in the binary oxide P even when calcined at the temperature as high as 1100 °C for 12 h. This means that the dispersions of Ti and Zr ions in the binary oxide A are extremely higher than those in the binary oxide P. The high dispersions of Ti and Zr ions in the binary oxide A were evidenced by EPMA measurements (see Fig. 5). It has been already proved by EXAFS (extended X-ray absorption fine structure) study[9] that the binary oxide A is predominantly composed of fine TiO_2 and ZrO_2 crystallites and that the binary oxide P mainly consists of large TiO_2 and ZrO_2 ones.

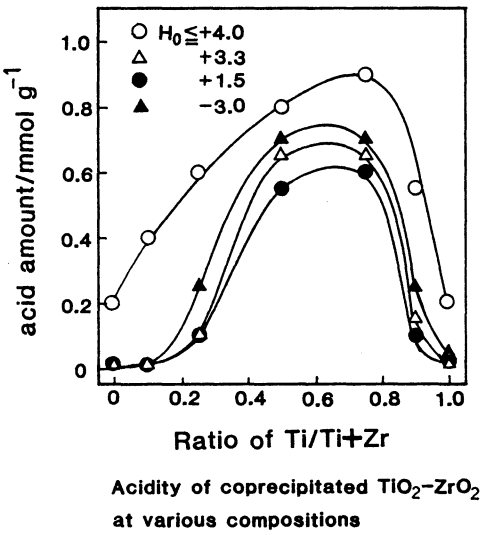


Fig. 7. Acid amounts with various acid strengths on the binary oxide A calcined at 650 °C.

Thus, a lot of Ti-O-Zr structures are expected at the interface between fine TiO_2 and ZrO_2 crystallites in the binary oxide A. It has been widely accepted that mixed oxide powders consisting of fine respective oxide crystallites often showed new acid sites originated from the generation of new bonding, M(1)-O-M(2), where M(1) and M(2) represent metal ions in the mixed oxide powders.[2] TiO_2-ZrO_2 system has been reported a typical case to generate new acid sites when the respective oxide crystallites are so small.[10] Indeed, the acid amount over 1 g of the binary oxide A was higher than that of the oxide P at any TiO_2/ZrO_2 ratios employed. (see Fig. 6a) While, as shown in Fig. 6b, the acid amounts over unit surface area of the binary oxide P is observed rather higher than those of the binary oxide A. Although the results might not be favorable for the opinion above, it is difficult to obtain rigid conclusions concerning the difference in the acid properties of the binary oxide A and P because of the ambiguity of the acid amounts measured in this work. No acid sites with $H_0 \leq +3.3$ were observed over the surface of binary oxide P, while considerable amounts of the acid sites with $H_0 \leq +3.3$ were generated on the surface of

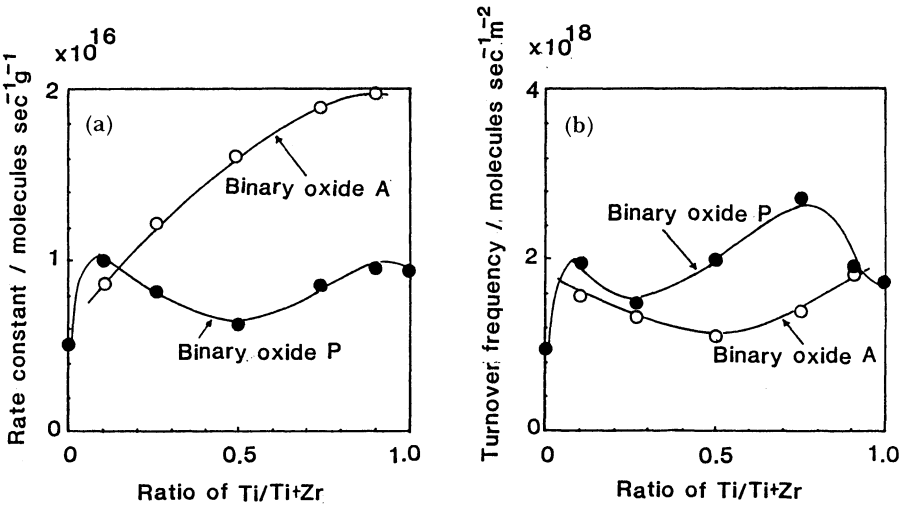


Fig. 8. a) Catalytic activities of binary oxides A and P expressed in terms of molecules·g^{-1}·s^{-1}; the catalysts were calcined at 650 °C before the reaction. b) Catalytic activities of binary oxidea A and P expressed in terms of molecules·m^{-2}·s^{-1}; the catalysts were calcined at 650 °C before the reaction.

binary oxide A, as shown in Fig. 7. Consequently, the total amounts of acid sites with $H_0 \leq +4.0$ over the binary oxide A might be the same as that on the binary oxide P, but the acid sites generated on the binary oxide A are much stronger than those on the binary oxide P. This probably due to the formation of Ti-O-Zr bonding over the binary oxide A[2] with a timid suspect whether the Ti-O-Zr bondings are merely required to generate a new and strong acid site. It must be mentioned that the acid amount, containing strong acid sites with $H_0 < +3.3$, on the binary oxide prepared by coprecipitation of a mixed solution of Ti and Zr tetrachlorides were observed almost the same as that on the binary oxide A. No significant effects of chlorine ions contaminated upon the acid property were recognized.

Recently, it has been reported that the binary oxide composed of fine TiO_2 and ZrO_2 particles is a potential catalyst for nonoxidative dehydrogenation of ethylbenzene to styrene.[3] It has been proposed that the reaction requires bifunctional sites, where one acts as an acid and the other acts as a basic site.[3] The high potential of the binary oxide for the dehydrogenation of ethylbenzene has been explained in terms of the generation of Ti-O-Zr bonding in the binary oxide, Ti ions being proposed to act as base and Zr ions as acid.

The nonoxidative dehydrogenation of ethylbenzene on the binary oxides A and P prepared in the present work was carried out at 620 °C to examine the role of Ti-O-Zr bonding during the reaction. The conversions of ethylbenzene and the selectivities to styrene over various catalysts are summarized in Table 2. From these results the rate constants and turnover frequencies were estimated assuming the first order with respect to ethylbenzene. As could be seen in Fig. 8a the rate constants over the binary oxide A expressed in terms of molecules $\cdot g^{-1} \cdot s^{-1}$ are observed to be higher than those over the binary oxide P. While the turnover frequency, given in Fig. 8b, showed the opposite results; turnover frequencies over the oxide A are rather smaller than those over the oxide P. If the dehydrogenation of ethylbenzene would take place on the bifunctional sites originated from Ti-O-Zr bonding over the catalyst surface, the results above means that almost the same or rather less amounts of Ti-O-Zr bonding are present over the unit surface area of the binary oxide A than on the binary oxide P. This is inconsistent with the idea that a lot of Ti-O-Zr bonding are on the surface of binary oxide A. In order to interpret this problem it might be favorable to deduce the conclusion that dehydrogenation of ethylbenzene would occur on the sites exposed on the surface of TiO_2 and ZrO_2 particles as well as on the sites composed of Ti-O-Zr bonding and that the reaction rate might not be so different in these active sites.

Thus, Ti-O-Zr bonding in TiO_2-ZrO_2 may not play an important role for nonoxidative dehydrogenation of ethylbenzene, being opposited to the previous opinion.[3]

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