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Decomposition of 2-Butanol Catalyzed by Iron Oxide and Mixed Oxides Containing Iron

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Three types of binary oxides, Fe_2O-TiO_2, Fe_2O_3-ZrO_2, and Fe_2O_3-ZnO, were prepared by a coprecipitation method, and their catalytic behaviors in the decomposition of 2-butanol were examined. The activities and selectivities of the catalysts varied with the type of the oxide with which Fe_2O_3 was combined, with the content of Fe_2O_3 in the binary oxides, and with the reduction temperature of the catalysts. Over the Fe_2O_3-TiO_2 catalysts, 2-butanol underwent primarily dehydration and the activity decreased with an increase in Fe_2O_3 content. Over the Fe_2O_3-ZnO catalysts, dehydrogenation preferentially occurred, the maximum activity being observed for the catalyst containing 67% Fe_2O_3. The Fe_2O_3-ZrO_2 catalysts exhibited an intermediate nature between the Fe_2O_3-TiO_2 catalysts and Fe_2O_3-ZnO catalysts. Reduction of catalysts tended to increase the dehydrogenation selectivity. Reduction also brought about the formation of butane. The maximum formation of butane was observed when the catalysts were reduced with hydrogen at about 350—400 °C. The reaction mechanisms of the formation of butane were elucidated by tracer experiments, and it was concluded that butane was formed by the mechanism involving the first order nucleophilic substitution (S_N1) of OH^- by H^- which was liberated in the dehydrogenation of butanols.

The catalysts containing iron have been used in various reactions such as ammonia synthesis, Fischer-Tropsch synthesis, water gas shift reaction, dehydrogenation of hydrocarbons, and oxidation reactions.[1] Meanwhile, combination of two types of oxides has been known to result in generation of acidic properties in many cases.[2] The acid-base properties of the catalysts containing iron, however, have not extensively been studied. Decomposition of 2-butanol generally yields butenes by dehydration over acidic catalyst and yields ethyl methyl ketone by dehydrogenation over basic catalyst.[3] Therefore, decomposition of 2-butanol seems to be an appropriate diagnostic reaction to see the acidic and basic properties of the catalysts. In the present work, variations in the catalytic activities and selectivities of the catalysts containing iron were examined as functions of catalyst composition, of reduction temperature and of types of oxides with which Fe_2O_3 was combined.

As previously reported, the formation of butane was observed during decomposition of 2-butanol over Fe_2O_3 catalyst.[4] In order to elucidate the reaction mechanism of the formation of butane, tracer experiments were also undertaken.

Table 1. Compositions and surface areas of catalysts

Nomenclature	Composition Fe/(Fe+X)/%[a]	Surface area m^2 g^{-1}
TiO_2	0	42
Fe_2O_3-TiO_2(1/9)	10	62
Fe_2O_3-TiO_2(1/3)	25	42
Fe_2O_3-TiO_2(1/1)	50	38
Fe_2O_3-TiO_2(7/3)	70	40
Fe_2O_3-TiO_2(9/1)	90	21
ZrO_2	0	64
Fe_2O_3-ZrO_2(1/9)	10	77
Fe_2O_3-ZrO_2(3/7)	30	112
Fe_2O_3-ZrO_2(1/1)	50	96
Fe_2O_3-ZrO_2(7/3)	70	53
Fe_2O_3-ZrO_2(9/1)	90	36
ZnO	0	5
Fe_2O_3-ZnO(2/9)	18	10
Fe_2O_3-ZnO(2/1)	67	27
Fe_2O_3-ZnO(18/1)	95	14
Fe_2O_3	100	16

a) X represents Ti, Zr, or Zn.

Experimental

Catalyst Preparation. The Fe_2O_3-TiO_2 catalysts with different compositions were prepared by hydrolysis of mixed solutions of ferric nitrate and titanium tetrachloride in different molar ratios with aqueous ammonia, the final pH being 8—9. The Fe_2O_3-ZrO_2 catalysts and the Fe_2O_3-ZnO catalysts with different compositions were similarly prepared from mixed solutions of iron(III) nitrate and zirconium nitrate or zinc nitrate. The precipitates obtained by the hydrolysis were washed with deionized water, dried at 100 °C for 20—30 h, and finally calcined at 500 °C in air for 2—3 h. The compositions, surface areas and nomenclatures of the resulting catalysts are given in Table 1.

X-Ray Diffraction. X-Ray diffraction patterns were measured with powdered samples on a Toshiba GD-3 diffractometer, the radiation source being Ni-flltered Cu $K\alpha$. For the samples reduced with hydrogen, the sample was cooled to room temperature under a helium stream, and slowly exposed to air to prevent the sample from rapid oxidation.[5,6]

Hydrogen Consumption during Reduction. The amounts of hydrogen consumed during reduction at different temperatures were measured for the Fe_2O_3 catalyst, the Fe_2O_3-ZrO_2 (7:3) catalyst, the Fe_2O_3-ZnO (2:1) catalyst, and the Fe_2O_3-TiO_2 (7:3) catalyst by use of a recirculation system of a small volume, 40 ml. The sample (0.1 g) was placed in a U tube and outgassed at 500 °C for 2 h. After cooling the sample to room temperature, hydrogen (200 Torr, 1 Torr = 133.3 Pa) was introduced in the system and circulated in the loop which was attached by a liquid nitrogen trap. The temperature of the sample was raised to 250 °C and kept at the temperature for 30 min. The amount of hydrogen consumed for reduction of the sample was measured by decrease in the pressure. Then the sample was heated stepwise by 50 °C increment to 500 °C. At each increment, the temperature was kept for 30 min.

Reaction Procedures. For the kinenic measurement of decomposition of 2-butanol, a microcatalytic pulse reactor was employed. A catalyst (0.1 g) was placed in a U-tube reactor and pretreated in a helium stream at 500 °C for 2 h. The catalyst was then cooled to the reaction temperature of 250 °C in a helium stream. In experiments with reduced catalysts, the catalysts were pretreated in a hydrogen stream for 30 min before cooling to the reaction temperature. The flow rate of helium was adjusted to 75 ml/min. 2-Butanol (10 μl) was injected by a syringe into a helium stream ahead of the catalyst. The reaction products were once trapped in a liquid nitrogen and flash-evaporated into gas chromatographic columns. The columns, PEG-20 M and VZ-7, were arranged in series for total analysis. By the former column operated at 80 °C, butenes plus butane, ethyl methyl ketone, and 2-butanol were separated. By the latter column operated at 0 °C, each isomer of butenes and butane were separated. The data of Figs. 2—5 and Table 4 were taken from No. 5 pulses which gave steady rates.

For carrying out some reactions, a closed recirculation reactor having a volume of 1280 ml was also employed. A catalyst (0.2 g) was outgassed at 500 °C for 2 h and reduced at 350 °C for 30 min by circulating hydrogen (150 Torr) in a loop of the reactor which was equipped with a trap of liquid nitrogen temperature. The catalyst was then outgassed at 240 °C for 30 min. A mixture of 1-butene (16 Torr) and hydrogen (18 Torr) or a mixture of 1-butene (3 Torr) and 2-propanol (27 Torr) was allowed to react at 242 °C over the Fe_2O_3 catalyst.

Two tracer experiments were also carried out in a closed recirculation reactor. One tracer experiment was the reaction of a mixture of 2-butanol (16 Torr) and deuterium (40 Torr). The other was the reaction of a mixture of monodeuterio 2-butanol ($CH_3CH_2CH(OD)CH_3$, 16 Torr) and heavy water (D_2O, 14 Torr). The isotopic distribution of butane was determined by mass spectrometry.

Results

X-Ray Diffraction. Crystalline structures detected by X-ray diffraction for the samples calcined at 500 °C in air are summarized in Table 2. For binary oxides of Fe_2O_3–ZrO_2 and Fe_2O_3–TiO_2, the crystalline structures detected were those of the mixture or one of the component oxides. New crystalline structures were not detected. For the Fe_2O_3–ZnO (2/9) and the Fe_2O_3–ZnO (2/1), a spinel structure of $ZnFe_2O_4$ was detected. All peaks detected for binary oxides calcined at 500 °C were weak in intensity and broad as compared with those for single component oxides.

Crystalline structures detected for the samples, Fe_2O_3, Fe_2O_3–ZrO_2 (7/3), Fe_2O_3–ZnO (2/1), and Fe_2O_3–TiO_2 (7/3), reduced with hydrogen at different temperatures

TABLE 2. CRYSTALLINE STRUCTURE OF THE CATALYSIS DETECTED BY XRD

Catalyst[a]	Observed spectra
TiO_2	TiO_2(sharp)
Fe_2O_3-TiO_2(1/9)	TiO_2(sharp)
Fe_2O_3-TiO_2(1/3)	TiO_2(broad), Fe_2O_3(very broad)
Fe_2O_3-TiO_2(1/1)	Fe_2O_3(very broad), TiO_2(very broad)
Fe_2O_3-TiO_2(7/3)	Fe_2O_3(broad)
Fe_2O_3-TiO_2(9/1)	Fe_2O_3
ZrO_2	ZrO_2(sharp)
Fe_2O_3-ZrO_2(1/9)	ZrO_2(sharp)
Fe_2O_3-ZrO_2(3/7)	ZrO_2(broad), Fe_2O_3(broad)
Fe_2O_3-ZrO_2(1/1)	Fe_2O_3(broad), ZrO_2(broad)
Fe_2O_3-ZrO_2(7/3)	Fe_2O_3(broad), ZrO_2(broad)
Fe_2O_3-ZrO_2(9/1)	Fe_2O_3(sharp)
ZnO	ZnO, (sharp)
Fe_2O_3-ZnO(2/9)	ZnO, $ZnFe_2O_4$(broad)
Fe_2O_3-ZnO(2/1)	$ZnFe_2O_4$(broad)
Fe_2O_3-ZnO(18/1)	Fe_2O_3(sharp)
Fe_2O_3	Fe_2O_3(sharp)

a) All the catalysts were calcined in air at 500 °C for 2 h.

TABLE 3. CRYSTALLINE STRUCTURE OF PRETREATED CATALYSTS DETECTED BY XRD

Catalyst	Temp of H_2 treatment	Observed spectra
Fe_2O_3	Untreated	Fe_2O_3(sharp)
Fe_2O_3	250 °C	Fe_3O_4, Fe(trace)
Fe_2O_3	350 °C	Fe(trace), Fe_3O_4(trace)
Fe_2O_3	500 °C	Fe(sharp)
Fe_2O_3-ZnO(2/1)	Untreated	$ZnFe_2O_4$(broad)
Fe_2O_3-ZnO(2/1)	250 °C	ZnO(broad), Fe_3O_4(trace), Fe(trace)
Fe_2O_3-ZnO(2/1)	350 °C	ZnO, Fe(trace), FeO(trace)
Fe_2O_3-ZnO(2/1)	500 °C	Fe(sharp), ZnO(sharp)
Fe_2O_3-ZrO_2(7/3)	Untreated	Fe_2O_3(broad), ZrO_2(broad)
Fe_2O_3-ZrO_2(7/3)	250 °C	ZrO_2(broad), Fe_3O_4(tract)
Fe_2O_3-ZrO_2(7/3)	350 °C	ZrO_2(broad), Fe_3O_4(trace), FeO(trace)
Fe_2O_3-ZrO_2(7/3)	500 °C	Fe(sharp), ZrO_2(sharp)
Fe_2O_3-TiO_2(7/3)	Untreated	Fe_2O_3(broad)
Fe_2O_3-TiO_2(7/3)	250 °C	Fe_3O_4(trace)
Fe_2O_3-TiO_2(7/3)	350 °C	Almost nothing
Fe_2O_3-TiO_2(7/3)	500 °C	Fe(sharp)

are summarized in Table 3. By reduction at 250 °C, the pattern of Fe_2O_3 disappeared and the pattern of Fe_3O_4 appeared for all samples, though all peaks for the binary oxides were broad and weak. By raising the reduction temperature to 500 °C, the patterns of oxide forms of Fe such as Fe_2O_3, Fe_3O_4, and FeO diminished and the sharp patterns of metallic Fe appeared. The spinel structure, $ZnFe_2O_4$, in the Fe_2O_3-ZnO (2/1) sample disappeared on reduction at 250 °C.

Hydrogen Consumption during Reduction. The amounts of hydrogen consumed in reduction of the Fe_2O_3, Fe_2O_3-ZrO_2 (7/3), Fe_2O_3-ZnO (2/1), and Fe_2O_3-TiO_2 (7/3) are plotted against the reduction temperature in Fig. 1. The easiness of reduction of these samples is in the following order:

$Fe_2O_3 > Fe_2O_3$-ZrO_2 (7/3) $> Fe_2O_3$-ZnO (2/1) $>$ Fe_2O_3-TiO_2 (7/3).

Assuming that a part of Fe^{3+} ions were reduced only to Fe^{2+} ions at 350 °C for all samples, the percentages of Fe^{3+} ions reduced to Fe^{2+} ions were calculated to be 50, 43, 32, and 22% for the Fe_2O_3, Fe_2O_3-ZrO_2 (7/3), Fe_2O_3-ZnO (2/1), and Fe_2O_3-TiO_2 (7/3), respectively. Since reduction of Ti^{4+} ions might occur to some extent for the Fe_2O_3-TiO_2 (7/3), the value, 22% is the maximum percentage of Fe^{3+} ions converted to Fe^{2+} ions.

Effects of Reduction of Catalysts on Activity and Selectivity for Reaction of 2-Butanol. Reaction of 2-butanol gave ethyl methyl ketone, butenes, and butane. The rate of conversion of 2-butanol and the product distribution varied with type of binary oxide and with pretreatment condition of catalysts. The percentage conversions of 2-butanol and the molar percentages of each product are plotted against the reduction temperature of catalysts in Figs. 2—5 for the Fe_2O_3 catalyst, the Fe_2O_3-ZrO_2 (7/3) catalyst, the Fe_2O_3-ZnO (2/1) catalyst, and the Fe_2O_3-TiO_2 (7/3) catalyst, respectively.

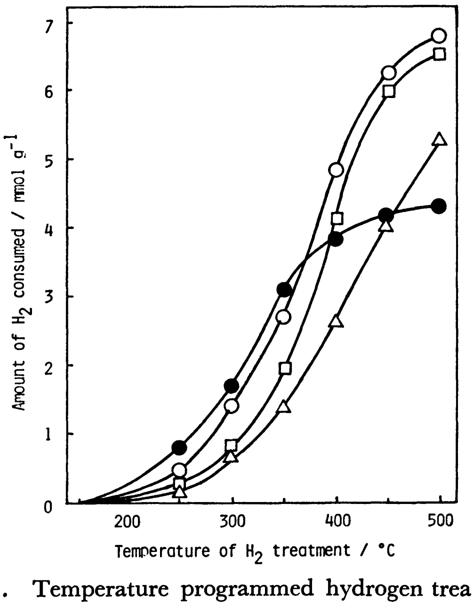


Fig. 1. Temperature programmed hydrogen treatment of iron oxide and binary oxides.
For binary oxides, the values of ordinate are based on 1 g of Fe_2O_3 contained in the catalysts. ●: Fe_2O_3, ○: Fe_2O_3-ZrO_2 (7/3), □: Fe_2O_3-ZnO (2/1), △: Fe_2O_3-TiO_2 (7/3).

With the Fe_2O_3 catalyst, the main product was ethyl methyl ketone over the whole range of the reduction temperature. The conversion of 2-butanol exhibited a maximum at the reduction temperature of 300 °C, and the ketone yield exhibited a maximum at the reduction temperature of 250 °C. It should be noted that considerable amounts of butane were produced when the catalyst was reduced in the temperature range of 300—400 °C. The formation of butane became maximum at the reduction temperature

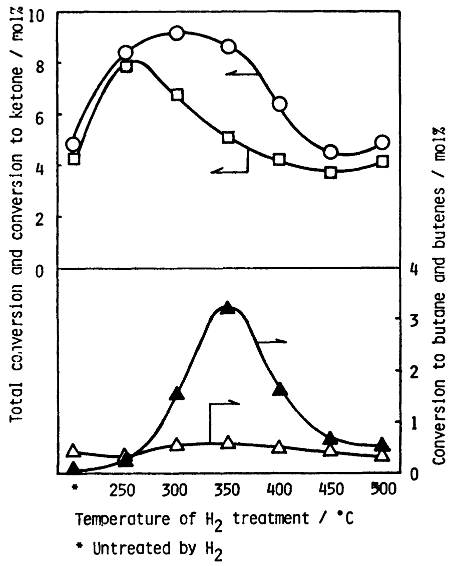


Fig. 2. Decomposition of 2-butanol over Fe_2O_3 at various temperatures of H_2 treatment.
Reaction at 250 °C with 0.1 g catalyst. ○: Total conversion, □: ketone, ▲: butane, △: butenes.

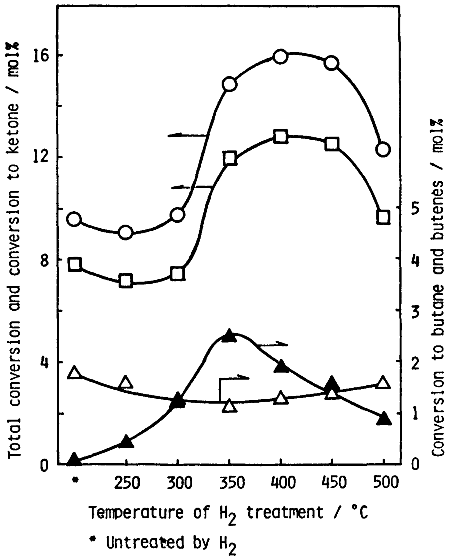


Fig. 3. Decomposition of 2-butanol over Fe_2O_3-ZrO_2 (7/3) at various temperatures of H_2 treatment.
Reaction at 250 °C with 0.1 g catalyst. ○: Total conversion, □: ketone, ▲: butane, △: butenes.

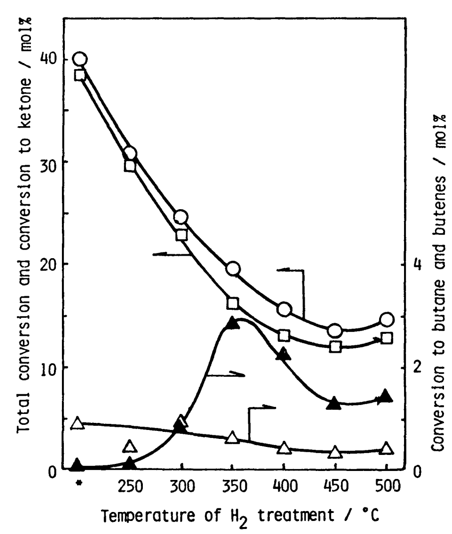


Fig. 4. Decomposition of 2-butanol over Fe_2O_3-ZnO (2/1) at various temperatures of H_2 treatment. Reaction at 250 °C with 0.1 g catalyst. ○: total conversion, □: ketone, ▲: butane, △: butenes.

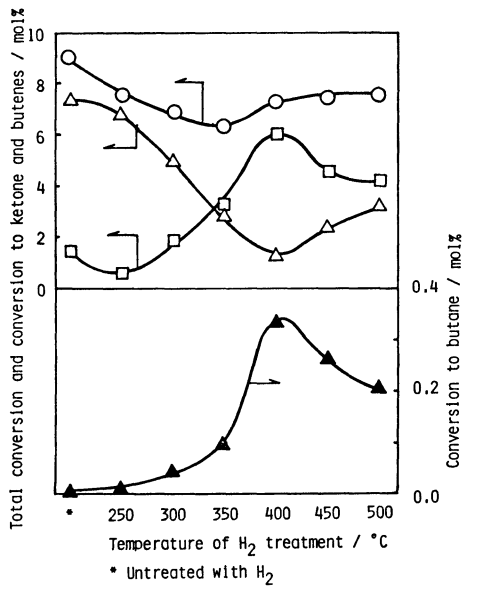


Fig. 5. Decomposition of 2-butanol over Fe_2O_3-TiO_2 (7/3) at various temperatures of H_2 treatment. Reaction at 250 °C with 0.1 g catalyst. ○: Conversion, □: ketone, ▲: butane, △: butenes.

of 350 °C.

With the Fe_2O_3–ZrO_2 catalyst, the main product was ethyl methyl ketone. The conversion of 2-butanol showed a maximum at the reduction temperature of 400 °C. The formation of butane was also observed over the wide range of the reduction temperature, 250—500 °C. The maximum formation was observed when the catalyst was reduced at 350 °C.

With the Fe_2O_3–ZnO (2/1) catalyst, the main product was also ethyl methyl ketone. The conversion of 2-butanol decreased steadily with an increase in the reduction temperature. The formation of butane reached maximum when the catalyst was reduced between 300—500 °C.

With the Fe_2O_3–TiO_2 (7/3) catalyst, the conversion of 2-butanol was almost independent of the reduction temperature. However, the ratios of ethyl methyl ketone/butenes changed much with the reduction temperature. When the reduction temperature was below 300 °C, butenes were produced much more than ethyl methyl ketone. On the contrary, ethyl methyl ketone was produced much more than butenes as the reduction temperature exceeded 350 °C. The amount of butane formed was less than 5% of total products, which was small as compared with the other catalysts. The maximum formation of butane was observed at the reduction temperature of 400 °C.

Activity and Selectivity of Catalysts with Different Compositions for Reaction of 2-Butanol. Product distributions in the reaction of 2-butanol over the binary oxides with different compositions and the component oxides are given in Table 4, in which the results both for the catalysts unreduced and for one reduced at 350 °C are included.

With unreduced Fe_2O_3–ZrO_2 catalysts, the dehydrogenation activities markedly increased as Fe_2O_3 was added to ZrO_2. The dehydration activities decreased with an increase in Fe_2O_3 content. The formation of butane was not observed. With the Fe_2O_3–ZrO_2 catalysts reduced at 350 °C, the maximum conversion of 2-butanol and activity for dehydrogenation were observed for the Fe_2O_3–ZrO_2 (1/1) catalyst. The formation of butane became maximum for the Fe_2O_3–ZrO_2 (7/3) catalyst.

With the unreduced Fe_2O_3–ZnO catalysts, the conversion of 2-butanol and the dehydrogenation activity became maximum for the Fe_2O_3–ZnO (2/1) catalyst. The dehydration activities were low, and the formation of butane was not appreciable for any compositions of the catalysts. With the reduced Fe_2O_3–ZnO catalysts, the conversion of 2-butanol and the dehydrogenation activity became maxima for the Fe_2O_3–ZnO (2/1) catalyst. The dehydration activity decreased as the content of Fe_2O_3 increased. The formation of butane was considerable and increased with an increase in the Fe_2O_3 content.

With the unreduced Fe_2O_3–TiO_2 catalysts, the dehydration activity decreased with an increase in the Fe_2O_3 content. The dehydrogenation activity became maximum for the Fe_2O_3–TiO_2 (1/1) catalyst. The formation of butane was not observed. With the reduced Fe_2O_3–TiO_2 catalysts, the dehydration activities decreased with an increase in Fe_2O_3 content. The dehydrogenation activity showed a maximum for the Fe_2O_3–TiO_2 (1/1) catalyst. The activities of the reduced Fe_2O_3–TiO_2 catalysts for the formation of butane were generally low as compared with those of the reduced Fe_2O_3–ZrO_2 catalysts and of Fe_2O_3–ZnO_2 catalysts.

Reaction of 1-Butene with Hydrogen. The compositions of the products in the reaction of 1-butene with H_2 over the Fe_2O_3 catalyst reduced at 350 °C are given in Table 5. The hydrogenation of butenes to butane was slow, the rate being 2.9×10^{-6} mol min^{-1} g^{-1}.

Reaction of 1-Butene in the Presence of 2-Propanol. The result for the reaction of a mixture of 1-butene and 2-propanol over the Fe_2O_3 catalyst reduced at

TABLE 4. PRODUCT DISTRIBUTION IN REACTION OF 2-BUTANOL

Catalyst	Conversion/%[a]	Butane/%[a]	Butenes/%[a]	Ketone/%[a]
TiO_2	32.5(18.0)	0.1(0.1)	31.9(17.8)	0.1(0.1)
Fe_2O_3-TiO_2(1/9)	22.5(18.6)	0.1(0.2)	22.0(16.6)	0.4(1.7)
Fe_2O_3-TiO_2(1/3)	14.6(14.3)	0.0(0.1)	11.3(12.4)	3.3(1.8)
Fe_2O_3-TiO_2(1/1)	16.2(17.4)	0.0(0.2)	11.2(12.8)	5.0(4.4)
Fe_2O_3-TiO_2(7/3)	8.6(7.1)	0.0(0.1)	7.2(3.8)	1.4(3.2)
Fe_2O_3-TiO_2(9/1)	2.6(3.7)	0.0(0.1)	1.8(1.0)	0.8(2.6)
ZrO_2	5.6(7.9)	0.0(0.0)	5.4(7.8)	0.2(0.1)
Fe_2O_3-ZrO_2(1/9)	11.9(9.6)	0.0(0.1)	6.5(4.3)	5.4(5.2)
Fe_2O_3-ZrO_2(3/7)	11.4(12.4)	0.0(0.7)	2.8(2.9)	8.4(8.8)
Fe_2O_3-ZrO_2(1/1)	10.5(13.6)	0.0(0.8)	2.4(1.7)	8.0(11.1)
Fe_2O_3-ZrO_2(7/3)	8.8(10.7)	0.0(2.4)	2.0(1.2)	6.8(7.1)
Fe_2O_3-ZrO_2(9/1)	4.8(7.0)	0.0(1.2)	0.8(0.8)	4.0(5.0)
ZnO	10.4(7.0)	0.0(0.0)	0.2(0.0)	10.2(9.0)
Fe_2O_3-ZnO(2/9)	13.9(17.9)	0.0(1.0)	1.3(1.7)	12.6(15.2)
Fe_2O_3-ZnO(2/1)	35.1(20.8)	0.0(3.2)	1.4(0.8)	33.7(16.8)
Fe_2O_3Z-ZnO(18/1)	5.1(11.4)	0.0(3.6)	0.5(0.3)	4.6(7.5)
Fe_2O_3	4.7(9.4)	0.0(3.8)	0.6(0.7)	4.1(4.9)

a) The data without parentheses represent the values over 0.1 g of unreduced catalysts, and thoses in parentheses are the values over 0.1 g of reduced catalysts.

TABLE 5. REACTION OF 1-BUTENE(6 TORR) IN H_2(18 TORR) OVER Fe_2O_3

Reaction temp	Reaction time	Conversion	Product yield/%		
			Butane	*t*-2-Butene	*c*-2-Butene
°C	min	%			
242	20	84.3	2.8	50.5	31.0

350 °C is shown in Table 6. The products consisted of propane, propene, and acetone. Butane was not formed, though propane was produced.

Reaction of 2-Butanol in the Presence of Deuterium. In the reaction of a mixture of 2-butanol and deuterium at 240 °C over the Fe_2O_3 catalyst reduced at 350 °C, monodeuteriobutane (butane-d_1) and dideuteriobutane (butane-d_2) were formed in addition to nondeuteriated butane. The percentages of butane-d_1 and butane-d_2 in total isotopic butanes are plotted against the conversion to butane in Fig. 6. Extrapolation to zero conversion gives nearly zero percentage for both the butane-d_1 and butane-d_2. The rate of the formation of butane was 4.0×10^{-6} mol min^{-1} g^{-1}, which was higher than the hydrogenation of 1-butene, 2.9×10^{-6} mol min^{-1} g^{-1}.

Reaction of Deuterio 2-Butanol-d in the Presence of Heavy Water. When a mixture of $CH_3CH_2CH(OD)CH_3$ and D_2O was allowed to react at 240 °C over the Fe_2O_3 catalyst reduced at 350 °C, formation of butane-d_1 was observed in addition to that of nondeuteriated butane. In Fig. 7, the percentage of butane-d_1 in total butane products is plotted against conversion of 2-butanol. Extrapolation to the zero conversion gives less than 50% for butane-d_1 and approached to nearly zero percentage at the zero conversion.

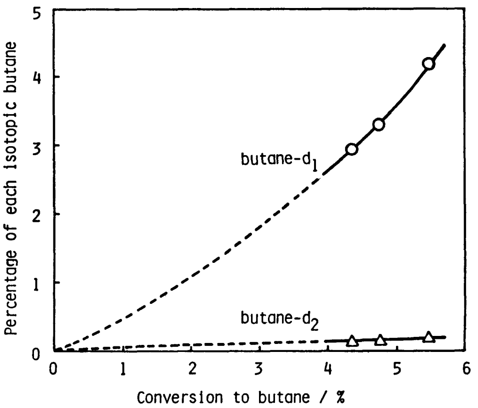


Fig. 6. Distribution of deuterated butane formed by reaction of 2-butanol with D_2. ○: butane-d_1, △: butane-d_2.

Discussion

X-Ray diffraction patterns of the binary oxides were generally weak and broad. The binary oxides consisted mostly of amorphous parts. By treatment with hydrogen, one component oxide, Fe_2O_3, was reduced and converted mainly to amorphous species. Metallic iron was considerably yielded by raising the temperature to 500 °C. The reduction became difficult when Fe_2O_3 was mixed with the other oxides; ZrO_2,

TABLE 6. REACTION OF MIXTURE 1-BUTENE AND 2-PROPANOL OVER Fe_2O_3[a)]

Reaction time	Composition of products/%					
min	1-Butene	2-Propanol	Propane	Propene	Acetone	Butane
0	10.00	90.00	0	0	0	0
40	10.06	64.87	1.53	0.56	22.98	0
70	10.07	50.18	2.17	0.99	36.59	0

a) The initial pressures of 1-butene and 2-propanol are 3 and 27 Torr, respectively.

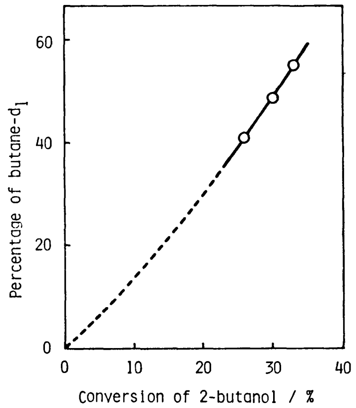


Fig. 7. Distribution of deuterated butane formed by reaction of 2-butanol with D_2O.

ZnO, and TiO_2. The difficulty of reduction of Fe_2O_3 in the binary oxides depended on the kinds of the other component oxides. There should be some chemical interactions between Fe_2O_3 and the other component oxides.

As for the activity and selectivity of the unreduced binary oxides, the catalytic properties of each component oxide seem to reflect on the activity and selectivity of the corresponding binary oxide catalysts. The catalytic properties of TiO_2 and ZrO_2 favored the dehydration, while those of ZnO and Fe_2O_3 favored the dehydrogenation. The binary oxides, Fe_2O_3–TiO_2 of any compositions and Fe_2O_3–ZrO_2 (1/9) mainly formed butenes, while Fe_2O_3–ZnO of any compositions and Fe_2O_3–ZrO_2 (3/7—9/1) gave ketone preferentially. It should be noted that a marked increase in the ketone yield was observed for the Fe_2O_3–ZnO (2/1) catalyst as compared with each component oxide.

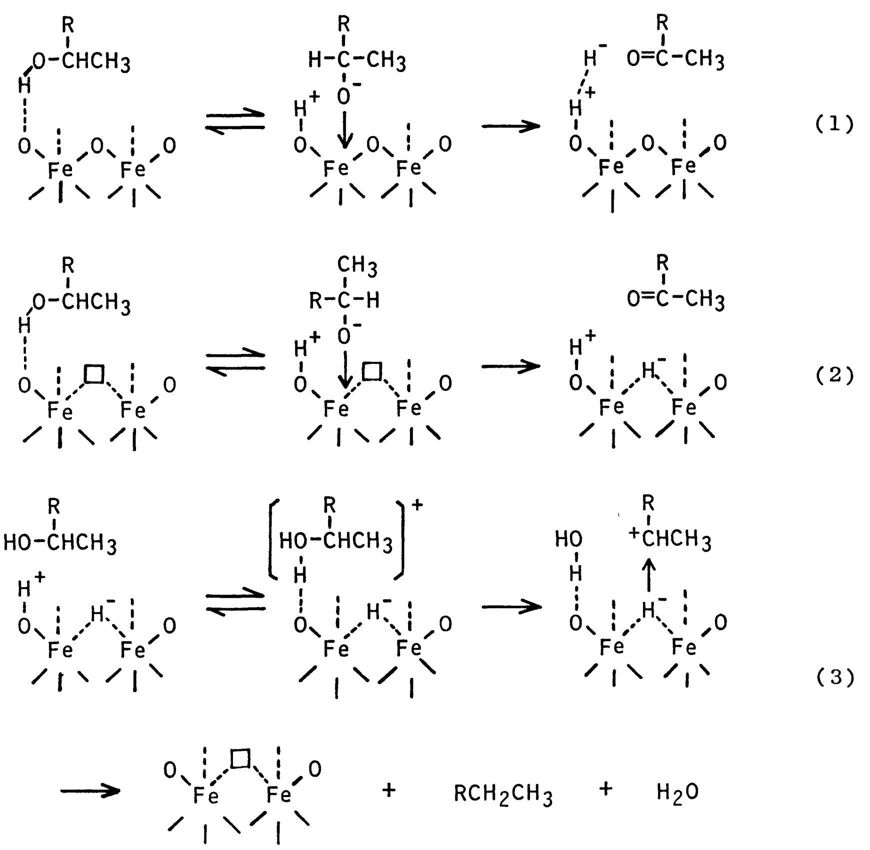
Reduction of the catalysts brought about obvious changes in both the selectivity and activity. Direction of the changes depended upon types of the binary oxides. One of the factors to control the selectivity in decomposition of alcohols is an acid-base properties of catalyst.[3)] With acidic catalysts, the dehydration predominantly takes place, while, with basic catalysts, the dehydrogenation proceeds. Changes in the dehydration and dehydrogenation selectivity of the binary oxides suggest that the acidic and basic properties of the catalysts change with the reduction state of Fe_2O_3 in the binary oxides. The change was especially marked for the Fe_2O_3–TiO_2 (7/3) catalyst. It appears that the basic property of the Fe_2O_3–TiO_2 (7/3) catalyst was strengthened by reduction above 350 °C.

The most prominent change in the selectivity occurred on reduction was the appearance of the formation of butane. For the catalysts, Fe_2O_3, Fe_2O_3–ZnO (2/1), Fe_2O_3–ZrO_2 (7/3), and Fe_2O_3–TiO_2 (7/3), the reduction temperatures which gave maximum formation of butane were 350, 350, 350, and 400 °C, respectively. These temperatures are close to the temperatures which were required to reduce Fe_2O_3 in those catalysts to Fe_2O_{3-x} (x=0.5) as seen in Fig. 1. Besides, these temperatures are also the temperature at which most of Fe_2O_3 in the catalysts converted to an amorphous species. Although the amounts of butane formed on unit amount of Fe_2O_3 in the binary oxides were not the same for different binary oxides, the amorphous iron oxide formed by the reduction seems to be the active species for the formation of butane.

The formation of butane from 2-butanols was observed over TiO_2 for the first time by Vinek *et al.*[7)] However, the activity of the reduced Fe_2O_3 for the formation of butane is much higher than that of TiO_2 as shown in Table 4.

Several possibilities are considered as to the reaction mechanism of the formation of butane. Hydrogenation of butenes which were produced by dehydration of 2-butanol with hydrogen which resulted from dehydration would be one of them. However, the rate of hydrogenation of 1-butene was lower than that of the formation of butane from 2-butanol. In addition, the presence of hydrogen had no marked effect on the rate of butane formation from 2-butanol.[4)] Therefore, hydrogenation of butene should be ruled out. Another possibility that butenes are hydrogenated by use of adsorbed hydrogen atoms or ions which are formed by the dehydrogenation of 2-butanol might be taken into account. If the formation of butane from 2-butanol occurred *via* butene, the formation of propane from 2-propanol would also occur *via* propene. If this is the case, the reaction of a mixture of 1-butene and 2-propanol would yield both butane and propane, since propene undergoes hydrogenation only 1.5 times faster than 1-butene does.[8)] The observed results showed that propane was produced, while butane was not produced (Table 5). This rules out the possibility that butane was formed through butenes by use of adsorbed hydrogen.

Vinek *et al.*[7)] proposed on the basis of higher reactivity of 1-butanol as compared with 2-butanol that butane was formed *via* the second order nucleophilic substitution (S_N2) of OH^- by H^-. They concluded that the source of the H^- nucleophile is water which results from the dehydration of butanols, as they did not take into account the adsorbed H^- which results



Scheme. Reaction scheme over Fe_2O_3 and reduced Fe_2O_3.

from the dehydrogenation.

In the present work, we propose that butane is formed *via* the first order nucleophilic substitution (S_N1) and that the H^- nucleophile is provided by the dehydrogenation of butanols. If the nucleophilic substitution proceeded by the S_N2 mechanism, 1-butanol would be easier to form butane than 2-butanol. If the substitution proceeded by the S_N1 mechanism, 2-butanol would undergo reaction much faster than 1-butanol. Our previous data[4] have shown that 2-butanol was easier to form butane than 1-butanol over the Fe_2O_3–ZrO_2 (7/3) catalyst. This suggests that the operating mechanism over the catalyst containing Fe_2O_3 is the first order nucleophilic substitution (S_N1) mechanism rather than the S_N2 mechanism.

The source of hydrogen would be either water[7] which results from dehydration or hydrogen which results from dehydrogenation. The amount of ethyl methyl ketone exceeded those of butane for all catalysts, whereas the amounts of butenes were lower than those of butane in the cases of some catalysts, Fe_2O_3, Fe_2O_3–ZnO (2/1—18/1), and Fe_2O_3–ZrO_2 (7/3—9/1) as seen in Table 4. It is, therefore, likely that the H^- nucleophile is supplied by the dehydrogenation of 2-butanol, but not from water. This is also supported by the percentage less than 50 of deuteriobutanes in total butane produced by the reaction of a mixture of the 2-butanol-*d* ($CH_3CH_2CH(OD)CH_3$) and heavy water, because if the hydride ion came from water formed from $CH_3CH_2CH(OD)CH_3$, the extrapolation to zero conversion should give 50% butane-d_1.

No incorporation of deuterium atoms into the butane molecules in the initial stage of the reaction of a mixture of 2-butanol and deuterium (Fig. 6) suggests that the hydrogen acting as the hydrogen source does not originate from molecular hydrogen, but from the adsorbed hydrogen which results from dehydrogenation of 2-butanol.

The reaction mechanism of the formation of butane could be drawn as follows. When dehydrogenation of alcohol occurs over the iron oxide catalyst, the alcohol dissociates into proton and alkoxide ion to adsorb on the catalyst surface at first, followed by losing of α hydrogen as hydride ion to form ketone (Scheme 1 or 2). The α hydrogen can be abstracted either by a proton or by an oxygen vacancy on the surface.[9] With the unreduced catalyst, the α hydrogen can be abstracted by H^+ (Scheme 1), since the metal ions are covered by oxygen atoms. In the case of the reduced catalyst, however, the α hydrogen tends to be abstracted as a hydride ion by an oxygen vacancy formed by reduction (Scheme 2). An alcohol molecule comes to the surface on which H^+ and H^- coexist and an alkoxonium ion is formed by the addition of H^+ to the alcohol. Since the present reaction was ascertained to proceed by the S_N1 mechanism, the alkoxonium ion must dissociate to form an alkyl cation. An alkane is produced by the nucleophilic attack of H^- to the alkyl cation (Scheme 3).

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