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FORMATION OF BUTANE FROM BUTANOL CATALYZED BY Fe_2O_3, Fe_2O_3-ZrO_2, AND Fe_2O_3-ZnO

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A considerable amount of butane was found to form from 1-butanol or 2-butanol over Fe_2O_3, Fe_2O_3-ZrO_2, and Fe_2O_3-ZnO at 250°C. The effect of hydrogen addition on the formation of butane was small. The mechanism is suggested to involve a nucleophilic substitution of OH^- by H^- which is liberated in the dehydrogenation of butanols.

Alcohols undergo dehydration to yield olefins over acidic catalysts and dehydrogenation to yield ketones or aldehydes over basic catalysts.[1)] Very recently alkanes have been reported to form from the correspondent alcohols over TiO_2.[2)] In the present work, we wish to report that Fe_2O_3, Fe_2O_3-ZrO_2, and Fe_2O_3-ZnO showed much higher activities than TiO_2 for the formation of butane from butanols.

The catalysts except Fe_2O_3-SiO_2 were prepared from each solution of $Fe(NO_3)_3\cdot 9H_2O$ and $TiCl_4$ or the mixed solutions of $Fe_2(NO_3)_3\cdot 9H_2O$ with $ZrO(NO_3)_2\cdot 2H_2O$, $ZnCl_2$, and $TiCl_4$, respectively, by precipitation or coprecipitation with ammonia water. The final pH was 8-9. The precipitates were washed with distilled water, dried at 100°C for 20-30 h and calcined at 500°C in air for 2-3 h. For preparation of Fe_2O_3-SiO_2, a mixed solution of aqueous $Fe_2(NO_3)_3$ and an alcoholic solution of ethyl orthosilicate was hydrolyzed by addition of ammonia water until the pH became 8. The precipitate was washed, dried at 100°C for 2 days and calcined at 500°C in air for 2-3 h. The content of Fe_2O_3 was 50 molar % in Fe_2O_3-SiO_2 and 70 molar % in all the other binary oxides. The reaction of 1-butanol or 2-butanol was carried out at 250°C in He or H_2 flow with a microcatalytic pulse reactor. In each run, 0.1 g of catalyst was used. Prior to the reaction, the catalysts were pretreated at 300°C in a hydrogen flow for 30 min.

The results are summarized in Table 1, where the data at the fifth pulse are shown. When 2-butanol was allowed to react, the main product over Fe_2O_3, Fe_2O_3-ZrO_2 and Fe_2O_3-ZnO, was methyl ethyl ketone, whereas the main product over Fe_2O_3-SiO_2, Fe_2O_3-TiO_2, and TiO_2 was butenes. With Fe_2O_3, Fe_2O_3-ZrO_2, and Fe_2O_3-ZnO, hydrocarbons were produced in addition to methyl ethyl ketone and, in particular, a considerable amount of butane was produced. The activity per unit surface area of catalyst for the formation of butane was highest in the case of Fe_2O_3, and followed by Fe_2O_3-ZnO, and Fe_2O_3-ZrO_2, while the formation of butane was not appreciable over Fe_2O_3-TiO_2, and TiO_2. The ability of Fe_2O_3, Fe_2O_3-ZnO, and Fe_2O_3-ZrO_2 to form butane was much higher than that of TiO_2 that has been reported to be only one

Table 1. Percentages of the Products in the Reaction of 1-Butanol or 2-Butanol over Fe-Containing Binary Oxides, Fe_2O_3, and TiO_2

Catalyst	Carrier	Reactant	Ketone or aldehyde[a]	Butane	1-Butene	trans-2-Butene	cis-2-Butene	Total conversion
Fe_2O_3-TiO_2	He	2-BuOH	1.90(0.46)[b]	0.05(0.01)	1.55(0.39)	0.97(0.24)	2.44(0.60)	6.91(1.70)
Fe_2O_3-ZnO	He	2-BuOH	23.5 (8.80)	0.61(0.23)	0.69(0.26)	0.06(0.02)	0.10(0.04)	24.9 (9.35)
Fe_2O_3-ZrO_2	He	2-BuOH	7.30(1.28)	1.17(0.21)	0.74(0.13)	0.11(0.02)	0.16(0.03)	8.48(1.67)
Fe_2O_3-ZrO_2	He	1-BuOH	0.51(0.09)	0.38(0.07)	0.03(0.01)	0	0	0.92(0.17)
Fe_2O_3-ZrO_2	H_2	2-BuOH	20.7 (3.64)	1.57(0.27)	0.76(0.13)	0.12(0.02)	0.17(0.03)	23.4 (4.09)
Fe_2O_3-ZrO_2	H_2	1-BuOH	2.77(0.49)	0.63(0.11)	0.45(0.08)	0.04(0.01)	0.05(0.01)	3.94(0.70)
Fe_2O_3-SiO_2	He	2-BuOH	1.85(0.06)	0.19(0.01)	6.4 (0.20)	9.92(0.30)	15.4 (0.47)	33.7 (1.04)
TiO_2	He	2-BuOH	0.06(0.01)	0.08(0.02)	3.45(0.82)	2.96(0.71)	7.87(1.88)	14.4 (3.44)
TiO_2	He	1-BuOH	0	0.08(0.02)	0.22(0.05)	0.01(0.00)	0.03(0.01)	0.34(0.08)
Fe_2O_3	He	2-BuOH	6.76(4.83)	1.49(1.06)	0.33(0.24)	0.14(0.10)	0.21(0.15)	8.84(6.38)

a; Ketone and aldehyde were formed in the reactions of 2-butanol and 1-butanol, respectively.
b; Percentages normalized to a 1 m^2 of catalyst basis are shown in paretheses.

oxide catalyst to form butane.2)

1-Butanol produced less amount of butane than 2-butanol over Fe_2O_3-ZrO_2. However, the selectivity for butane was higher in 1-butanol than in 2-butanol, about 93 % of the hydrocarbons produced from 1-butanol being butane. When 2-butanol and 1-butanol were reacted over Fe_2O_3-ZrO_2 in a hydrogen flow, the hydrocarbon products increased by 1.2 times and 2.9 times, respectively. However, the amount of butane increased by only 1.3 times and 1.6 times, respectively. The percentages of butane in hydrocarbons increased from 54 % to 60 % in the case of 2-butanol, while it decreased from 93 % to 54 % in the case of 1-butanol.

If the formation of butane resulted entirely from the secondary hydrogenation of primarily formed butenes, the amount of butane or the percentage of butane in hydrocarbon would greatly increase either in the case of 1-butanol or 2-butanol when the reaction was carried out in a hydrogen carrier. This was not the observed case. A small increase in the amount of butane in a hydrogen carrier may suggest that the formation of butane by the hydrogenation of butenes may be included to a small extent. However, there should be the other main mechanism to produce butane. For the formation of butane from 1-butanol on TiO_2, Venek et al proposed a nucleophilic substitution(S_N-2) of OH^- by H^-, where the H^- was originated from water that is produced in dehydration of the alcohol. In the present cases, the reaction mechanism for the production of butane can be speculated as follows. A mechanism that butane forms from alcohols mainly by a nucleophilic substitution of a hydroxyl ion in alcohols by a hydride ion seems to be very likely in the present case on the basis of hydrogen effect over Fe_2O_3-ZrO_2. In the nucleophilic substitution mechanism, the source of a hydride ion may be heterolytically adsorbed hydrogen that produced in the dehydrogenation of butanols.

References

1) O. V. Krylov, "Catalysis by Non-metals", Academic Press, New York, 1970.
2) H. Vinek, J. Lercher, and H. Noller, Proc. 7th Intern. Congr. Catalysis, 1980 Tokyo, Part B, p. 1456, Elsevier, 1981.

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