The Selective Synthesis of But-2-ene from Ethanol over Alumino-Borate B–C_1 Catalyst

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Alumino-borate B–C_1 catalyst pretreated at 573 K showed effective activity (20–40%) and selectivity (>60%) in the formation of but-2-ene from ethanol and diethyl ether at 523–573 K.

Recently, a series of crystalline alumino-borate (B-C_n) have been synthesized.[1,2] These materials have unique, novel three-dimensional framework structures with triangular BO_3, tetrahedral BO_4 and AlO_4 as their basic building units. Efforts are being made in our laboratory to demonstrate their potential as new catalysts for chemical reactions. Ethanol, which can be easily produced from cane sugar and biomass, is becoming an energy source and a raw material for synthesis of various chemicals. Among the chemicals, ethylene,[3] buta-1,3-diene[4] and acetone[5] are selectively synthesized over heterogeneous catalysts. In the present communication we report that the first member of B–C_n alumino-borate, B–C_1, is an effective catalyst for a selective synthesis of but-2-ene from ethanol and diethyl ether at 523–573 K. It will be emphasized that the unique structure of B–C_1 is essential for the high selectivity of but-2-ene.

B–C_1 was synthesized according to the molar ratios of $0.75B_2O_3:3.0Al_2O_3:2.5NH_4OH:1000H_2O$. A weighed amount of boric acid and aluminium trichloride were dissolved in distilled water. Aqueous ammonia was then added under stirring and a hydro-gel formed. Finally, the pH of the mixture was adjusted to 3.5 with Et_3N solution, and the reaction was further stirred for 1 h.

Crystallization of the reaction mixture was carried out in a stainless steel autoclave under autogeneous pressure at 473 K for 3 days. The crystalline product was filtered, washed with anhydrous ethanol and dried at ambient temperature, followed by calcination in air at 573 K for 3.5 h. The sample thus obtained has a composition of $B_2O_3/Al_2O_3 = 0.015$ (molar ratio) by both chemical analysis and X-ray photoelectron spectroscopy measurement. Fig. 1 shows the X-ray diffraction pattern of the B–C_1 catalyst. Loss of crystallinity was observed after calcination at temperatures higher than 673 K. The IR spectrum of the adsorbed pyridine suggested that B–C_1 possesses only Lewis acid sites of moderate acid strength after calcination at 573 K.

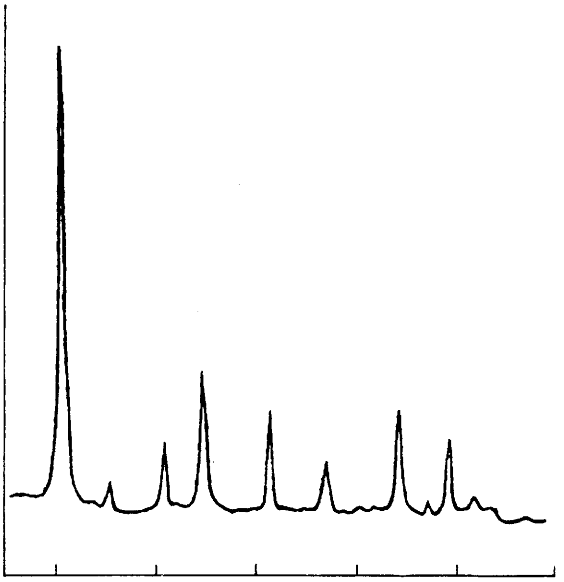

Fig. 1 X-Ray powder diffraction pattern of B–C_1 catalyst

Catalytic reactions were carried out with 0.1 g of the catalyst at 523–623 K by use of a conventional pulse micro-reactor positioned ahead of a GC column (Poropack QS) as described elsehwere.[6] The catalyst was pretreated at 573 K in stream of a carrier gas (He: ~25 ml min^{-1}) for 1.5 h before the catalytic reaction. Ethanol and diethyl ether (analytical grade) were used after drying over molecular sieves (4 Å). An injection of 1 μl was performed for each pulse. Product distribution was obtained by GC analysis and is expressed on a dry basis, *i.e.* exclusive of water product. A separate experiment was also performed by use of a mass analyser, instead of GC, as the detector. The results obtained are shown in Table 1. The catalyst exhibits an effective activity (~21%) for ethanol conversion at temperature as low as 523 K. A selective formation of but-2-ene (>60%) is outstanding at 523–573 K. Production of ethylene and acetaldehyde are below 5% though a considerable amount of diethyl ether is formed. The results of diethyl ether conversion are also given in Table 1. It is apparent that the product distribution of diethyl ether is similar to that of ethanol though the former reactant shows lower reactivity. Since it is possible to convert diethyl ether into but-2-ene under the same conditions, we calculate the selectivity of but-2-ene in products exclusive of diethyl ether product. The values in parentheses of Table 1 give this kind of selectivity which is above 90% at <573 K. The formation of but-2-ene decreases drastically while that of ethylene increases remarkably with rising temperature.

Fig. 2 shows the activity and selectivity changes in a sequence of pulses. The selectivity for but-2-ene in the products remains higher than 60% in all the pulses though it decreases with an increase in the pulse number. The decrease

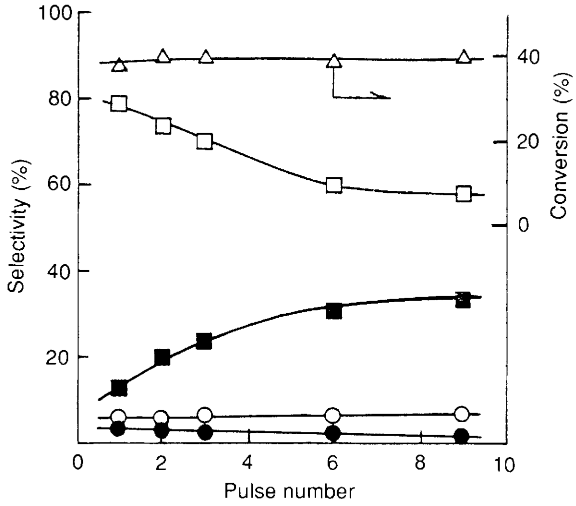

Fig. 2 Variation of activity and product selectivities with pulse number in ethanol conversion at 573 K. □: 2-C_4H_8; ■: Et_2O; ○: C_2H_4; ●: MeCHO

Table 1 Activity and product selectivity of B–C_1 catalyst for ethanol and diethyl ether conversion at different temperature

Reactant	Ethanol					Diethyl ether	
T/K							
Conversion	523	548	573	598	623	548	573
(%)	21.5	31.3	39.5	66.4	85.8	11.6	19.9
Product distribution, wt%							
C_2H_4	0.42	1.09	5.46	11.40	53.69	3.11	5.49
1-C_4H_8	—	trace	trace	trace	0.75	trace	trace
2-C_4H_8	60.88	76.43	73.45	65.44	38.03	89.92	85.04
	(98.72	97.91	91.13	84.49	40.67)[a]	(96.66	94.04)[b]
Et_2O	38.33	21.94	19.40	22.55	6.50	—	—
EtOH	—	—	—	—	—	6.97	9.57

[a] Selectivity exclusive of diethyl ether. [b] Selectivity exclusive of ethanol.

of but-2-ene is accompanied by an increase of diethyl ether product. Variation of the other products, ethylene and acetaldehyde, are insignificant. The reversed changes of but-2-ene and diethyl ether in Fig. 2 and the lower reactivity of the ether than ethanol (Table 1) might suggest that diethyl ether is an intermediate product in the ethanol to but-2-ene reactions.

Study on the effect of pretreatment temperature on the catalytic behaviour of B–C_1 showed that the samples pretreated at 723 and 973 K catalysed selectively the formation of ethylene (>90%) from ethanol. Since a complete change of the crystalline structure of B–C_1 is revealed by framework vibrational spectra (IR) and XRD measurements of these two samples, it is concluded that the unique crystalline structure of B–C_1 is essential for the high selectivity of but-2-ene.

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