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BUTADIENE YIELDS IN THE REACTIONS OF BUTENES OVER BINARY LIQUID ALLOY CATALYSTS CONTAINING K OR Na

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Three liquid alloy catalysts, K-In, K-Pb and Na-Pb, are active for the dehydrogenation of butenes, giving 1,3-butadiene. These catalysts are also active for isomerization and decomposition but an appropriate choice concerning the catalyst, the reactant butene and the reactant partial pressure minimizes the decomposition and improves the reactant recovery.

Since little is known[1)] about the catalytic activities of molten metal or molten alloy catalysts for the reaction of a straight chain hydrocarbon, the authors have attempted to throw some lights on this problem. In view of an industrial importance the reactions of butenes have been examined in the present work.

The catalytic activity was measured using a flow type apparatus with a bubbling type reactor[2)]. The making and purification[3)] of the catalyst alloy were carried out in a vessel filled with dry helium, and a pure portion of the alloy liquid was transferred from the alloy preparation vessel to the reactor through a pipe line. 1-Butene, trans-2-butene and cis-2-butene were obtained commercially and used separately as the reactant. The purity of every reactant was better than 99.5 %.

Prior to the reaction the partial pressure of the reactant was adjusted to a desired value by mixing with helium. Then the mixture was made to contact with about 70 g of the liquid alloy catalyst, and the reaction products were analyzed with gas chromatography; HITACHI-MODEL-163 equipped with FID, column=sebaconitrile 10 m, temperature=30 °C, carrier gas=N_2 with a flow rate of 30 ml/min. A mass-spectrometer (JEOL-JMA-2000S) equipped with a gas chromatographic column (VZ-10,2 m) was used for the identification of 1,3-butadiene.

Exemplified in Table 1 are the experimental data obtained with the 5.9 %-K-In catalyst. The product distribution informs us that the overall reaction consists of three kinds of reactions, dehydrogenation (I), isomerization (II) and decomposition (III). Of course the reaction I formed 1,3-butadiene, and the products of the reaction II depended on the species of butenes reacted; trans- and cis-2-butene from 1-butene, 1-butene and cis-2-butene from trans-2-butene, 1-butene and trans-2-butene from cis-2-butene. The products of the reaction III also varied depending on the species of the reactant butenes; 1-butene decomposed to CH_4, C_3H_6, C_2H_4 and C_2H_6 while 2-butenes decomposed mainly to CH_4 and C_3H_6. The formation of hydrocarbons with carbon numbers higher than five was insignificant.

Table 1 Composition* of the gas produced in the reaction** over the K-In*** liquid alloy catalyst

Reactant	1-Butene						2-Butene	
							trans-	cis-
Temperature, ^{o}C	568	575	591	601	615	617	616	618
CH_4	0.9	1.2	2.1	3.0	5.0	5.4	2.3	2.5
C_2H_6 + C_2H_4	0.9	1.2	1.9	2.5	3.6	3.7	0.6	0.7
C_3H_8	t	t	t	t	t	t	t	t
C_3H_6	0.8	1.0	1.8	2.5	3.9	4.1	1.8	1.9
iso-C_4H_{10}	b	b	b	b	b	b	b	b
n-C_4H_{10}	b	b	b	b	b	b	b	b
1-C_4H_8	b	b	b	b	b	b	6.9	5.8
trans-2-C_4H_8	3.6	4.2	4.7	5.2	5.4	5.6	b	12.5
cis-2-C_4H_8	5.1	5.4	6.0	6.4	6.1	6.0	9.1	b
1,3-C_4H_6	6.5	7.7	9.0	9.6	10.7	10.6	8.5	10.0
Residues****	0.1	0.1	0.2	0.3	0.4	0.5	0.1	0.1

* in mole percent. ** The partial pressure of the reactant = 0.5 atm, and the feed rate of the reactant = 0.5 ml/sec. *** 5.9 atomic percent of K. **** C_5 or more higher hydrocarbons. t: trace. b: balance.

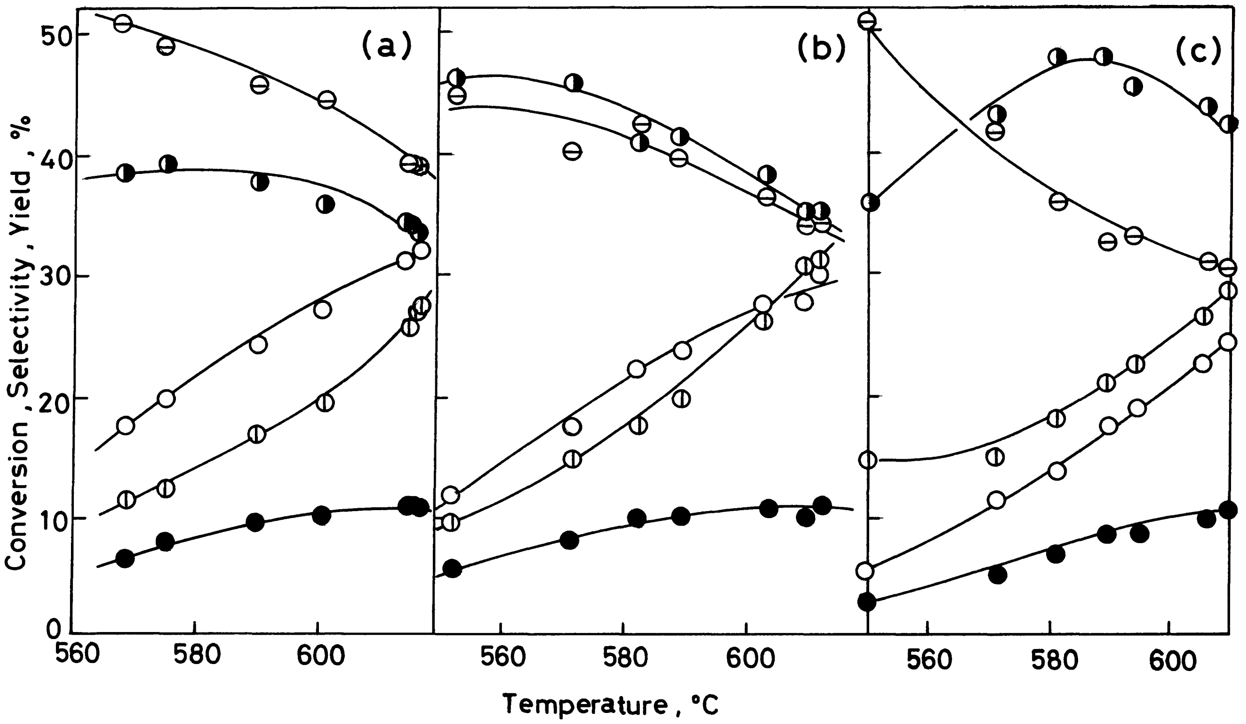

Fig. 1 Activities of the K-In (a), K-Pb (b) and Na-Pb (c) liquid alloy catalysts for the reaction of 1-butene; conversion to 1,3-butadiene (○); selectivities for the reactions I (◑), II (⊖) and III (⦶); yield of 1,3-butadiene (●).

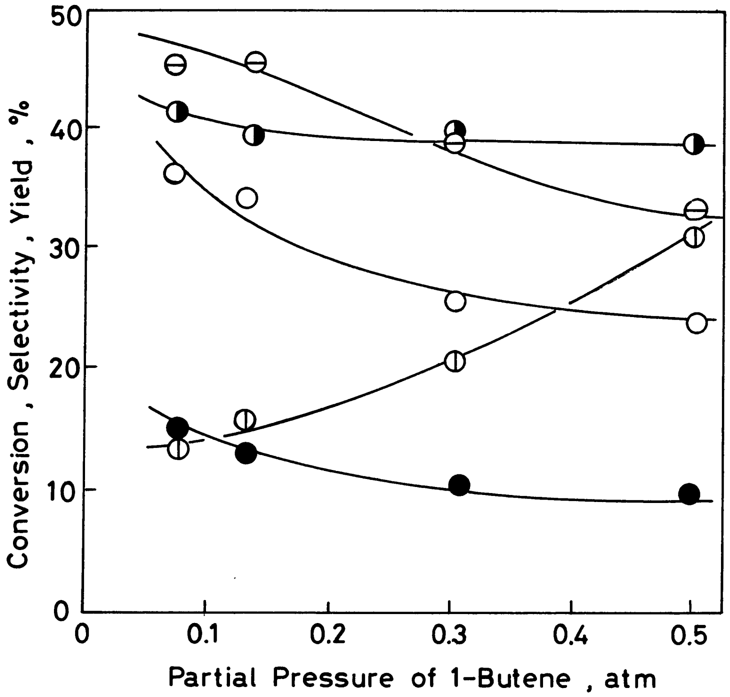

Fig. 2 Effects of partial pressure of 1-butene in the feed gas upon the reaction I, II and III; total conversion (○); selectivities for I (◑), for II (⊖), and for III (⦶); yield of butadiene (●). The total feed rate of gas = 1.0 ml/sec. Temp. = 620 °C. Catalyst = Na-Pb.

Table 2 Results* obtained with varying catalysts and varying reactants

Temperature, °C	616-618			612-613			610-612		
Catalyst	K-In			K-Pb			Na-Pb		
Butene reacted	1-	trans-2-	cis-2-	1-	trans-2-	cis-2-	1-	trans-2-	cis-2-
Total conv.	30.3	28.0	31.7	27.3	26.4	27.5	24.3	33.1	39.0
Butadiene yield	10.3	8.7	10.3	9.4	8.8	9.6	10.2	7.8	9.0
Selectivity of reaction									
I	34.0	31.1	32.4	34.4	33.4	34.9	42.0	23.7	23.0
II	39.4	58.4	59.4	34.8	54.3	55.8	30.0	68.1	72.4
III	26.6	10.5	8.2	30.8	12.3	9.3	28.0	8.2	4.6
Overall selectivity for C_4 olefins	73.4	89.5	91.8	69.2	87.7	90.7	72.0	91.8	95.4

* The values in this table are represented in %; the partial pressure of the reactant was 0.5 atm and the feed rate of every butene was 0.5 ml/sec.

The main features of the reactions over the other catalysts (30%-K-Pb, 50%-Na-Pb) were analogous to those mentioned above, though details were different.

From the practical point of view, the yield of butadiene and the recovery of the reactant deserve special attention.4) As can be seen in Fig. 1, every catalyst examined was capable to promote the formation of butadiene and its yield increased with the reaction temperature. However the temperature raise resulted in a promotion of the reaction III, which depressed the reactant recovery. The side reaction II, which was also significant at any reaction temperatures, would not cause the depression of the reactant recovery, because any butene isomers were convertible to butadiene over the liquid alloy catalyst. Therefore, it is of great importance to minimize the selectivity of III and elevate the overall selectivity of I + II.

There are two ways to suppress the unfavorable reaction III. As can be seen in Fig. 2, the reduction of the partial pressure5) of the reactant greatly suppressed the reaction III while the yield of butadiene was elevated. Another way is the use of either cis- or trans-2-butene as the reactant instead of 1-butene. The advantage of this way is best demonstrated by the data shown in Table 2. The combination of the Na-Pb catalyst with the cis-2-butene reactant best minimized the decomposition reaction III; in other words, a satisfactorily high overall selectivity for I + II was obtained.

References and Notes

1) Three papers reporting the activities for certain aromatic hydrocarbons were published; the last one is " K. Honda, K. Takahashi, Y. Saito and Y. Ogino, Chem. Lett., 1978, 693 " . Twelve papers reporting the activities for the reactions of alcohols and amines were published; the last one is " Y. Saito and Y. Ogino, J. Catal., 55, 198 (1978).

2) K. Kashiwadate, Y. Saito, A. Miyamoto and Y. Ogino, Bull. Chem. Soc. Japan, 44, 3004 (1971).

3) K. Honda and Y. Ogino, J.C.S. Chem. Comm., to be published.

4) The life of the catalyst will be also important; a laboratory use of two days did not deteriorate the catalytic activity.

5) K. Hoshiai, " Catalytic Engineering ", Catalysis Society of Japan ed., vol. 7, p. 176, Chijin Shokan, Tokyo (1964).

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