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NOTES

Reaction of Butadiene to Aromatics over Supported Catalysts

Although the gas phase dimerization of butadiene to 4-vinylcyclohexene and subsequent dehydrogenation of this product to ethylbenzene and styrene has been demonstrated using a variety of catalyst systems (*1*), little has been reported on the one-stage conversion of butadiene to aromatic hydrocarbons. Under mild conditions (300°C) the sole product of the uncatalyzed reaction is the Diels-Alder dimer (*2*) and elevation of the temperature to 500°C leads to a number of secondary reactions with low selectivity to simple aromatics (*3*). A Russian patent (*4*) claims the reaction of butadiene over γ-alumina at 500°C producing 76% selectivity to ethylbenzene at 35% conversion of butadiene, but this result could not be reproduced. Following reports on the use of cobalt oxide supported on charcoal as a catalyst for the dimerization–dehydrogenation of olefins (*5*), Yates and Wheatley (*6*) studied the reaction of butadiene in this system at 300°C. The liquid product consisted of simple aromatics but no attempt was made to increase the conversion from 28% w/w. We would like to report our findings on the reaction of butadiene over various heterogeneous catalysts under conditions leading to high butadiene conversion.

Most of the catalysts used were cation-exchanged mordenites. The mordenite was Norton Zeolon 20/50 mesh granules. This was supplied in the sodium form and was exchanged with various cations using conventional techniques giving a catalyst containing 1.5 to 2% metal. In the case of cobalt, studies have also been made using carbon, silica, alumina and silica-alumina as supports. The carbon used was 10–18 mesh charcoal supplied by B.D.H. The silica and alumina were supplied by Girdler and the silica–alumina by Crosfields. These supports were impregnated with cobalt nitrate which was decomposed thermally to cobalt oxide (*6*).

Butadiene (B.D.H.) and nitrogen (white spot) were used as supplied.

Reactions were carried out at atmospheric pressure by passing a preheated mixture of 10 ml min^{-1} butadiene and 10 ml min^{-1} nitrogen over catalyst (80 ml) heated to the required reaction temperature in a furnace. Before reaction the catalysts were heated under a nitrogen flow for several hours at the reaction temperature. The products were collected in solid carbon dioxide–isopropanol cooled traps and the catalyst tube was weighed before and after reaction.

The liquid analyses were carried out on a Becker 409 gas chromatograph using a 2 m 2% Dexil 300 H.P. chromosorb W AW DMCS (80–100) column (30°C for 20 min then to 150°C at 10°/min). The liquid products were initially identified by gas chromatography–mass spectrometry and subsequently checked by spiking samples with authentic compounds.

The residue on the catalyst was analyzed for carbon and hydrogen using a Perkin-Elmer 240 elemental analyzer.

TABLE 1

Products from Reaction of Buta-1,3-diene over 1.5% Cobalt on Various Supports[a]

	Mordenite	Alumina	Silica	1:3 Alumina–silica	Charcoal
% Conversion	69.4	86.2	86.0	79.9	72.3
% Selectivity to					
Benzene	4.4	6.2	4.7	0	0.4
Toluene	9.6	5.9	5.7	0.7	1.6
Xylenes	7.2	7.3	11.0	4.9	3.7
Ethylbenzene	41.4	16.3	24.5	3.7	2.0
Vinylcyclohexene	22.9	25.7	4.7	0.1	0
Higher aromatics	7.3	6.8	3.5	2.2	0.3
Volatiles	2.4	8.9	12.1	1.2	0
Solid	4.8	22.9	33.8	87.2	92.0

[a] 460°C, residence time 4 min (% wt).

TABLE 2

Products from Reaction of Buta-1,3-diene over Metal Cations Exchanged into Mordenite[a]

	Cobalt (II)	Nickel (II)	Zinc (II)	Copper (II)	Iron (II)	Tin (II)	Chromium (III)	Calcium (II)	Indium (III)	Sodium (I)[b]	Manganese (II)
% Conversion	76.0	72.0	67.4	30.6	100.0	76.6	77.8	43.9	80.6	64.0	65.9
% Selectivity to											
Benzene	5.7	6.1	5.5	5.4	4.3	4.6	4.6	1.8	4.4	3.7	3.6
Toluene	9.4	27.7	12.2	21.6	7.6	9.6	7.0	5.1	8.6	10.8	8.3
Xylenes	23.2	9.2	24.2	9.8	10.7	13.2	10.1	10.9	14.3	20.0	18.1
Ethylbenzene	39.3	32.9	35.6	32.9	37.3	22.6	20.5	33.4	14.1	9.6	33.0
Vinylcyclohexene	0	2.6	0	1.7	4.4	6.7	19.8	7.8	20.4	17.9	5.7
Higher aromatics	7.3	10.1	10.7	11.5	22.2	10.2	29.1	30.0	24.8	29.2	14.8
Volatiles	4.8	6.5	3.2	6.3	4.1	24.0	8.6	2.3	5.1	3.4	3.6
Solid	10.3	4.9	8.6	10.8	9.4	9.1	0.3	8.7	8.3	5.4	12.9
EtPh/higher arom.	5.38	3.25	3.33	2.86	1.68	2.21	0.70	1.11	0.57	0.33	2.23

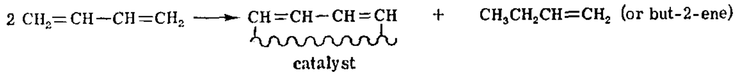
[a] 500°C, residence time 4 min.

[b] Unexchanged zeolite = 5.27% sodium.

The effect of catalyst support on the activity of cobalt is demonstrated in Table 1. The results obtained using various metals exchanged into mordenite are shown in Table 2.

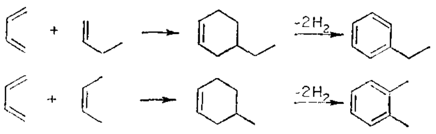
The higher aromatics consisted of a range of compounds including C3–C6 substituted benzenes and C1–C4 substituted naphthalenes. The solid residue left on the catalyst corresponded by microanalysis to a compound having a hydrogen-to-carbon ratio of 0:1. The volatile products were C4 hydrocarbons dissolved in the liquid phase.

The reaction mechanisms proposed by Yates and Wheatley (*6*) may be invoked to explain some of the products observed. In this mechanism the butadiene initially disproportionates to adsorbed diene and olefin:

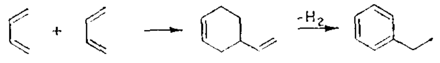


$$2\,CH_2{=}CH{-}CH{=}CH_2 \longrightarrow \underset{\text{catalyst}}{CH{=}CH{-}CH{=}CH} + CH_3CH_2CH{=}CH_2 \text{ (or but-2-ene)}$$

The olefins may react with butadiene to produce ethylbenzene and *o*-xylene:



The ethylbenzene may also result from dehydrogenation of 4-vinyl cyclohexene:



The *m*- and *p*-xylenes, benzene and toluene may be formed via the acid-catalyzed alkylation–dealkylation reactions known to occur under these conditions. The higher boiling products may result from the further reaction of the primary benzenoid products with olefinic, dienic and cationic fragments, and polymerization of dienes and olefins.

The lower proportion of solid material formed in the reaction using the zeolite support may be explained on structural grounds. Mordenite consists of two types of micropore, wherein the metal cation is sited. The smaller pore is only large enough for butadiene molecules, whereas the larger pore may contain molecules as large as triethylbenzene (*7*). Therefore only a small number of C_4 molecules can take part in a reaction at a catalytic site and other fragments cannot reach these sites to react further with the simple aromatics formed as primary products. No such restriction exists on the other supports and the adsorbed aromatic products are open to further attack.

In the experiments involving the change of cation on mordenite the amount of solid formed is again generally low, indicating that this is indeed a function of the support. The main difference lies in the ratios of ethylbenzene (derived from two C_4 fragments) to the higher aromatics. This ratio is highest with cobalt, copper, nickel and zinc and is probably due to the known ability of these metals to coordinate dienes, both singly and in pairs (*8*). Hence the diene pairs will react at the dimerization–dehydrogenation sites rather than the acidic silica–alumina sites. This work forms the basis of a patent application (*9*).

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