JOURNAL OF CATALYSIS 22, 427–429 (1971)

NOTE

Aromatization of Lower Olefins

A recent letter to the editor in this journal (*1*) reported a new catalytic reaction for the aromatization of lower olefins using a bismuth phosphate catalyst. This prompts us to report our results on aromatizing lower olefins.

In a previous paper (*2*) we reported that 1,5-hexadiene and benzene can be formed from propylene using a supported Bi_2O_3 oxidant. The concentration of benzene relative to 1,5-hexadiene increased with both temperature and contact time. However, at higher reaction temperatures and contact times, the stability of the Bi_2O_3 oxidant decreased due to reduction of the Bi_2O_3 to bismuth metal.

In an attempt to operate at lower temperatures, which minimizes the bismuth instability problem, and to obtain high aromatic formation, the use of a mixed oxidant–catalyst bed was evaluated. Such an oxidant–catalyst bed consisted of segregated Bi_2O_3–Al_2O_3 and Cr_2O_3–Al_2O_3 particles. The Bi_2O_3–Al_2O_3 oxidant would give predominantly olefin dehydrodimerization followed by Cr_2O_3–Al_2O_3 catalyzed dehydrocyclization.

The olefin-to-aromatic reaction reported here was carried out in the same apparatus as previously described (*2*). The methods of catalyst preparation and product analyses are also the same. The reaction was carried out cyclically with the olefin being passed over the bed for 10 min and then the catalyst–oxidant regenerated with air for 10 min at the same temperature. The effluent was analyzed every minute over the 10-min cycle and the value reported in Tables 1 and 2 were obtained after 5 min of reaction. The reaction was carried out using a downflow reactor with a bed consisting of randomly mixed Bi_2O_3–Al_2O_3 and Cr_2O_3–Al_2O_3 particles.

The data obtained for the conversion of propylene are given in Table 1. These data show the striking effect on selectivity when Cr_2O_3–Al_2O_3 is added to the bismuth oxidant. By adding 2 vol% Cr_2O_3–Al_2O_3, the selectivity to 1,5-hexadiene declines approximately 60%, the loss of selectivity being due to formation of 1,3-hexadiene, 1,4-hexadiene, and benzene. Further addition of Cr_2O_3–Al_2O_3 results in complete conversion of 1,5-hexadiene and a fairly constant composition of 1,3-hexadiene, 1,4-hexadiene, and benzene. There is little effect on product distribution by adding more Cr_2O_3–Al_2O_3 beyond 10 vol%, suggesting that a steady-state condition is obtained. It is interesting to note the low concentration of 2,4-hexadiene obtained when Cr_2O_3–Al_2O_3 is present. Evidently this isomer is rapidly converted to the cyclohexadiene isomers. Also the concentrations of these cyclohexadiene isomers are low, which is understandable since they are easily converted to benzene both thermally and oxidatively.

Data obtained from the reaction of isobutylene are given in Table 2. Again the abrupt effect on product selectivity by adding Cr_2O_3–Al_2O_3 can be seen from these data. With isobutylene a higher selectivity to cyclic intermediates is obtained compared to the cyclic intermediates formed from propylene under comparable conditions. Because of chromatographic separation difficulties, individual values of the dimethylhexadiene and dimethylcyclohexadiene isomers could not be assigned. It

TABLE 1

EFFECT OF VOL% CHROMIA-ALUMINA ON PRODUCT DISTRIBUTION FOR THE CONVERSION OF PROPYLENE[a]

Vol% of Cr_2O_3–Al_2O_3 in oxidant–catalyst bed[b]	Propylene conversion (Mol %)	Selectivity (mol %)									
		CO_2	Acrolein	2,4-H[c]	1,5-H	1,3-H	1,4-H	C_6H_6	1,3-CH[c]	1,4-CH	Other
0[d]	13.4	17.9	2.8	2.2	48.7	3.7	1.0	17.3	3.8	2.5	—
1.96	13.5	17.7	2.4	1.6	18.8	8.3	10.5	35.9	—	1.2	3.6
3.85	15.0	19.0	2.6	1.1	6.3	11.4	12.5	41.0	—	1.9	4.2
7.41	14.8	19.8	2.0	—	1.1	9.6	16.4	47.4	—	0.9	2.8
10.71	17.9	14.6	1.8	—	—	14.3	17.2	43.1	—	1.1	7.8
0[e]	15.9	19.2	3.0	2.3	43.2	3.7	1.0	20.6	3.7	3.4	—
1.96	16.4	20.2	2.5	1.5	15.0	8.8	8.8	38.6	—	1.4	3.1
3.85	18.2	17.3	2.0	1.2	5.2	10.6	13.6	44.9	—	1.8	3.5
7.41	17.8	20.1	1.9	—	1.6	10.0	14.7	46.1	—	1.1	4.4
10.71	23.2	14.4	2.8	—	—	12.3	15.0	45.0	—	2.6	7.9

[a] Temp = 540°C, propylene partial pressure = 0.9, atm, nitrogen other gas.

[b] Chroma-alumina catalyst contained 12% Cr_2O_3, 4% SiO_2, and 2% K_2O, 128 m^2/g, 10–20 mesh, 33.1 g. (25 cm^3) of 18 wt % Bi_2O_3 on Al_2O_3, 6–8 mesh.

[c] H = hexadiene, and CH = cyclohexadiene.

[d] Propylene flow rate = 76 cm^3/min.

[e] Propylene flow rate = 66 cm^3/min.

TABLE 2

EFFECT OF VOL% CHROMIA-ALUMINA ON PRODUCT DISTRIBUTION FOR THE CONVERSION OF ISOBUTYLENE[a]

Vol% of Cr_2O_3–Al_2O_3 in oxidant–catalyst bed[b]	Isobutylene conversion (mol %)	Selectivity (mol %)							
		CO_2	MA[c]	DI[c]	DMCH[c]	DMH[c]	*p*-Xylene	*m*-Xylene	*o*-Xylene
0[d]	14.9	25.9	7.0	4.7	18.0	17.8	21.4	2.2	0.9
9.1	14.2	27.9	2.4	4.5	6.6	8.5	46.4	3.0	0.1
12.5	14.7	26.5	2.2	2.5	4.4	9.6	52.2	1.8	0.1
15.4	15.7	22.5	1.5	3.6	3.2	12.3	54.4	1.4	0.1
0[e]	18.8	22.6	3.0	5.5	14.9	18.6	31.7	2.0	1.2
9.1	19.5	22.0	2.0	3.9	6.4	15.2	47.1	2.4	1.0
12.5	19.8	21.4	1.7	2.6	6.4	13.7	50.4	2.2	0.6
15.4	20.0	19.8	1.6	3.3	5.4	12.3	54.6	1.7	0.5

[a] Temp = 540°C, isobutylene partial pressure = 0.9 atm, nitrogen other gas.

[b] Twenty-three g (17.5 cm^3) 18 wt % Bi_2O_3 on Al_2O_3, 6–8 mesh.

[c] MA = methacrolein; DI = diisobutylene; DMCH = dimethylcyclohexadiene isomers; and DMH = dimethylhexadiene isomers.

[d] Isobutylene flow rate = 54 cm^3/min.

[e] Isobutylene flow rate = 46 cm^3/min.

is interesting to note the very high selectivity to *p*-xylene. This indicates that there is high retention of structure of the linear hexadiene and cyclohexadiene isomers as they pass through the oxidant–catalyst bed.

The conditions under which the propylene and isobutylene reactions were carried out are close to optimum based on experiments where various parameters were evaluated. The details of these experiments are beyond the scope of this note.

The large change in selectivity by adding Cr_2O_3–Al_2O_3 to the oxidant bed is not too surprising since at 2 vol% Cr_2O_3–Al_2O_3 the 1,5-hexadiene liquid hourly space time would be approximately 0.6 with respect to Cr_2O_3–Al_2O_3. This space time is close to that reported by Frilette and Haag (*3*) for the dehydrocyclization of 1,5-hexadiene, 2,5-dimethyl-1,5-hexadiene, and other nonconjugated dienes. The unique feature that permits aromatization of olefins via the system described in this note is that the temperature range for optimum dehydrodimerization and dehydrocyclization activities is about the same. Thus, only the amount of catalyst in the oxidant has to be varied to maximize aromatic formation. This system is similar in some respects to that reported by Nix and Weisz (*4*) for the conversion of heptane to toluene using a dual-function fluid catalyst consisting of a mechanical mixture of two different materials. In the latter work the relative rate of each function could also be adjusted by the amount of each component in the mixture. To obtain the full benefit of the individual compounds, particle sizes smaller than 100 μ were required. The use of particles in this size range permitted adequate diffusional flow of the gas phase intermediate or intermediates from one particle to another. In the work reported in this note smaller Bi_2O_3–Al_2O_3 and Cr_2O_3–Al_2O_3 particles could not be used because of prohibitively large pressure drops across the fixed bed. Fluidization could not be used because of high loss of Bi_2O_3 from the support by attrition.

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Received January 25, 1971