3. Proper selection of a noninteracting catalyst carrier is important to prevent thermal degradation. The $NiAl_2O_4$ coating appears to impart catalytic stability to the Pd–Ni catalyst system compared to Al_2O_3–SiO_2.

4. The optimum reaction conditions for NO reduction over Pd–Ni and Pd–Ru occur at air-to-fuel ratios just slightly rich of stoichiometry, an operating region also characterized by maximum power output and nearly minimum fuel consumption in the IC engine.

Acknowledgments

The author gratefully acknowledges stimulating discussions with and technical assistance by C. A. Leech, III, L. E. Campbell, R. L. Johnson, and J. A. Myers.

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Received for review May 13, 1974
Accepted September 25, 1974

Presented at the Third North American Meeting of the Catalysis Society, San Francisco, Calif., February 1974.

Synthesis of Cyclohexene, Cyclohexadiene, and Benzene *via* Disproportionation of Butadiene over Tungsten Oxide–Silica Catalyst

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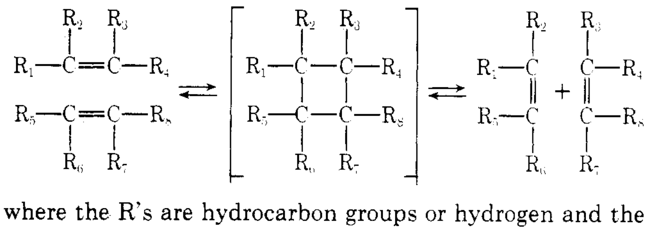
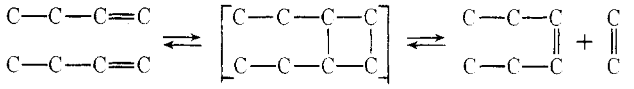
Cyclohexadiene and benzene were synthesized by disproportionating butadiene over tungsten oxide–silica catalysts at 500–550°C, atmospheric pressure, and 25 wt hourly space velocity. Cyclohexene was obtained by selective hydrogenation of cyclohexadiene. Relative selectivities to 1,3-cyclohexadiene and to benzene were a function of process conditions. At 515°C with catalyst containing 3% tungsten oxide, conversion of butadiene was 36%, selectivity to cyclohexadiene was 46% (62% of theoretical), and selectivity to benzene was 21%. At 550°C with 16% tungsten oxide catalyst, conversion of butadiene was 59% and selectivities to cyclohexadiene and benzene were 24 and 45%, respectively. Hydrogenation of 1,3-cyclohexadiene was near 100% selective to cyclohexene. About 4% of the butadiene thermally dimerized to vinylcyclohexene when 100% butadiene was used as the feed. Blending *n*-butane with the butadiene reduced the rate of dimerization. Coke deposited on the catalyst amounted to 1–2% of the converted butadiene. The butadiene disproportionation reaction provides a new route for the synthesis of cyclohexene, 1,3-cyclohexadiene, and benzene.

The catalytic conversion of monoolefins to approximately equal quantities of shorter and longer chain olefins has been studied intensely since this highly selective disproportionation reaction was first reported by Banks and Bailey (1964). The reaction is not limited to monoolefins; in 1969 we disclosed that dienes could also be disproportionated (Heckelsberg, *et al.*, 1969). Over an alkali-modified tungsten oxide–silica catalyst, 1,3-butadiene reacted with propylene to yield 1,3-pentadiene and ethylene, with isobutene to yield 4-methyl-1,3-pentadiene and ethylene, and with itself to yield cyclohexadiene and ethylene. The present paper reports results of additional studies of the disproportionation of butadiene to yield 1,3-cyclohexadiene. In addition to synthesizing cyclohexadiene, the reaction provides routes for producing cyclohexene and benzene from butadiene.

Mechanistic studies by a number of investigators and an abundance of data (Banks, 1972) indicate that the catalytic disproportionation of olefins proceeds by two unsaturated pairs of carbon atoms combining in a four-center transition state which dissociates by breaking the opposite set of bonds to form the new olefins. The reaction scheme can be pictured as



where the R's are hydrocarbon groups or hydrogen and the brackets indicate a transition state. An example is the disproportionation of 1-butene to 3-hexene and ethylene.



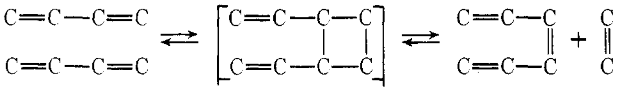
Selectivities above 90% have been reported for the above reaction.

Table I. Butadiene Disproportionation Tests over Tungsten Oxide–Silica Catalyst

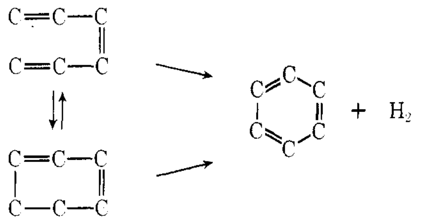
	Test number										
	1	2	3	4	5	6	7	8	9	10	11
Tungsten oxide–silica catalyst											
Tungsten oxide, wt %	8	8	8	8	8	8	3	3	3	12	16
Butadiene–butane feed											
Butadiene, wt %	100	38	37	42	40	40	40	50	40	40	39
Test conditions											
Temperature, °C	540	540	540	540	530	550	505	515	540	550	550
Pressure, psig	0	0	0	0	0	100	0	0	0	0	0
Space rate, g/g-hr	23	24	25	24	100	100	19	19	21	20	27
Butadiene conversion, %[a]	49.0	39.0	46.0	53.3	17.5	70.5	10.4	36.1	42.5	62.4	58.9
Product composition, wt %[a]											
Ethylene	5.1	8.3	7.1	5.4	12.8	6.2	12.3	13.9	18.6	8.0	8.5
Propylene	4.7	2.6	4.2	4.0	2.9	10.9	2.4	3.2	4.7	6.8	6.7
Butenes	13.6	1.3	1.2	1.3	4.3	4.4	(*b*)	2.1	2.3	1.6	1.8
Pentadienes	7.1	4.0	3.6	5.4	2.9	7.3	4.8	4.3	5.2	6.0	5.2
Cyclohexadiene	15.8	37.8	36.6	33.1	41.4	10.9	47.6	45.5	29.8	22.2	24.0
Benzene	37.5	36.5	38.4	38.4	21.4	27.6	7.1	21.4	32.0	43.0	44.6
Toluene	5.3	2.7	2.4	2.7	(*b*)	8.4	(*b*)	(*b*)	1.7	4.4	3.5
Vinylcyclohexene	7.3	4.0	3.5	3.6	14.3	10.2	23.8	8.6	2.9	1.6	0.9
Others	1.6	1.4	1.8	4.8	(*b*)	14.1	(*b*)	(*b*)	1.7	6.4	3.5
Coke	2.0	1.4	1.2	1.3	(*c*)		2.0	1.0	1.1		1.3
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

[a] Average of period, generally 2 hr, when conversion was highest. [b] Trace amounts. [c] Not determined.

If this reaction scheme were applied to the disproportionation of 1,3-butadiene, hexatriene and ethylene would be the products.



Experimentally, only trace quantities of hexatriene were found in the butadiene disproportionation products. However, 1,3-cyclohexadiene, an isomer of hexatriene, was a major C_6 product. This cyclization reaction can occur thermally (Lewis and Steiner, 1964). In the current investigation, benzene, the dehydrogenation product of cyclohexadiene, was also obtained.



A route for synthesizing cyclohexene is provided by partial hydrogenation of cyclohexadiene over a selective hydrogenation catalyst (Johnson, *et al.*, 1972) in a separate step.

Experimental Section

A continuous-flow system similar to those described previously (Heckelsberg, *et al.*, 1969; Banks and Regier, 1971) was used for the diene disproportionation tests. The fixed-bed reactor was constructed from a 15-in. section of ¼-in. stainless steel pipe. An electric furnace controlled the temperature of the reactor. The diolefin feed passed through a bed of 13X molecular sieves and downflow through the disproportionation catalyst. Liquid effluent from the reactor was collected in a trap at Dry Ice–acetone temperature. A small amount of gas effluent did not condense in the trap and was metered and vented.

The disproportionation catalysts were prepared by promoting silica gel with different levels of tungsten oxide (Heckelsberg, *et al.*, 1968). Prior to each test the catalyst was activated in the reactor with dry air at 540°C for 3 hr, heated in dry nitrogen to 600°C, and treated with hydrogen at 600°C for 1 hr. The activated catalyst was cooled under nitrogen to the temperature at which the diolefin feed was introduced into the reactor.

The feed blends were prepared from Phillips special or pure grade hydrocarbons. For most of the tests the feed was subjected to a mild hydrotreatment; the liquid feed was saturated with hydrogen at 70 psig and passed over a palladium–alumina catalyst at 180°C.

Analyses of feed blends and product samples were by gas–liquid chromatography. Infrared analyses and gas–liquid chromatography–mass spectroscopy were used for the identification of the products.

Results and Discussion

Presented in Table I are the results of 11 tests in which butadiene was disproportionated at various conditions over tungsten oxide–silica catalysts. The butadiene conversions are an order of magnitude greater than those reported for studies with alkali-treated tungsten oxide–silica catalyst (Heckelsberg, *et al.*, 1969). The product compositions are also different from the earlier study; in the present investigation, appreciable amounts of aromatics were produced and the yields of ethylene and of vinylcyclohexene were lower than reported previously.

Butadiene Concentration. The feed used in the first test shown in Table I was 100% butadiene. The test was at 540°C, atmospheric pressure, and 23 g of butadiene/hr/g of catalyst. Control of the temperature of the catalyst bed was difficult and the catalyst activity declined rapidly (49% conversion at 2 hr to 9% at 4 hr). A blank test with quartz chips in the reactor confirmed that some thermal dimerization of butadiene to vinylcyclohexene was occurring at these conditions. Improved temperature control of the catalyst bed was achieved by reducing the butadiene

Table II. Effect of Butadiene Concentration

	Butadiene in feed, wt %		
	100	38	37
Butadiene Conversion, %[a]	49.0	39.0	46.0
Yield, wt %[a]			
Cyclohexadiene	15.8	37.8	36.6
Benzene	37.5	36.5	38.4
Benzene + toluene	42.8	39.2	40.8
Vinylcyclohexene	7.3	4.0	3.5

[a] For period of highest activity.

Table III. Effect of Reaction Temperature on Butadiene Disproportionation

	Reaction temp, °C		
	505	515	540
Butadiene conversion, %	10.4	36.1	42.5
Yields, wt %			
Ethylene	12.3	13.9	18.6
Cyclohexadiene	47.6	45.5	29.8
Benzene + toluene	7.1	21.4	33.7
Vinylcyclohexadiene	23.8	8.6	2.9

Table IV. Effect of Catalyst Composition on Butadiene Disproportionation

	Catalyst, wt % WO_3			
	3	8	12	16
Temperature, °C	540	540	550	550
Butadiene conversion, %	42.5	53.3	62.4	58.9
Yields, wt %				
Cyclohexadiene	29.8	33.1	22.2	24.0
Benzene	32.0	38.4	43.0	44.6
Benzene + toluene	33.7	41.1	47.4	48.1
Vinylcyclohexene	2.9	3.6	1.6	0.9

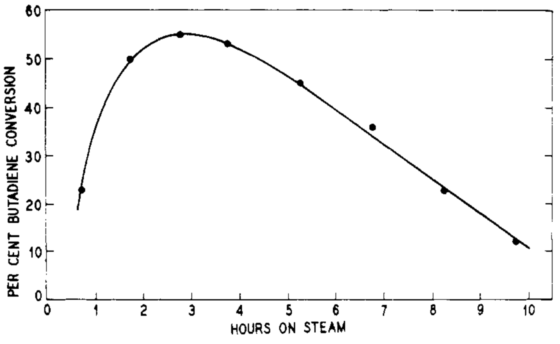


Figure 1. Butadiene conversion *vs.* time on stream.

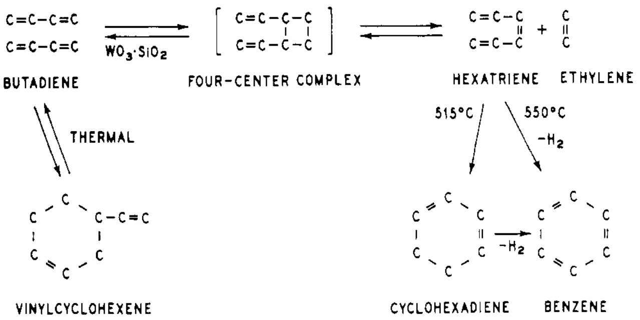


Figure 2. Reaction paths for the synthesis of cyclohexene, cyclohexadiene, and benzene from butadiene.

Table V. Synthesis of Cyclohexadiene and Benzene from Butadiene

	Catalyst, wt % WO_3	
	3	16
Feed, wt % butadiene	50	39
Reaction conditions		
Temperature, °C	515	550
Pressure, psig	0	0
WHSV	19	27
Butadiene conversion, %	36.1	58.9
Yields, wt %		
Cyclohexadiene	45.5	24.0
Benzene	21.4	44.6
Benzene + toluene	21.4	48.1

concentration in the reactor. Tests 2 and 3 were with butadiene–butane feed blends containing 62–63% normal butane. Conversion of butadiene in test 2 was 39% at 5 hr and decreased to 16% at 10 hr. With the paraffin diluent the thermal dimerization of butadiene to vinylcyclohexene was reduced and the yield of cyclohexadiene doubled. These results are summarized in Table II.

Feed Purification. Some improvement in the level of butadiene conversion was obtained by subjecting the butadiene–butane feed to a mild hydrotreatment step over palladium–alumina catalyst (test 4, Table I). However, the rates of decline in catalyst activity were about the same both without and with the hydrotreatment step.

Space Rate. The yield of cyclohexadiene was increased and the yield of aromatics reduced by increasing the space rate from 24 to 100 g of feed/hr/g of catalysts (test 5 compared to test 4). This change in contact time reduced butadiene conversion by a factor of 3 and increased dimer formation relative to the catalytic disproportionation reaction.

Reaction Pressure. A significant decrease in the yield of cyclohexadiene occurred when pressure in the reactor was increased from atmospheric to 100 psig (test 6). High butadiene conversions and good yields of aromatics were obtained during the first hour of operation; however, catalyst activity decreased rapidly and, after 2 hr, thermal dimerization was the predominant reaction.

Reaction Temperature. Butadiene conversion and yields of aromatics and ethylene increased when reaction temperature was increased from 505 to 540°C (Table I, tests 7, 8, and 9). The yields of cyclohexadiene and of vinylcyclohexene decreased. Conversion and yield data for these tests are summarized in Table III.

Catalyst Composition. The tungsten oxide content of the disproportionation catalyst was varied from 3 to 16 wt %. As shown in Table IV, the yield of aromatics increased with increased tungsten oxide content of the catalyst. Yields of cyclohexadiene were highest with the 3 and 8% tungsten oxide catalysts; however, part of the differences in yields can be attributed to difference in the temperatures of these tests.

In another experiment, a nickel–silica catalyst was mixed with the tungsten oxide–silica to promote the dehydrogenation of cyclohexadiene to benzene. The yield of aromatics was increased about 20%, with a corresponding increase in conversion.

Catalyst Activity. A catalyst induction period was observed for most of the tests. In general, the highest activity of the catalyst was not obtained until after about 2 hr on stream. The activity then declined with time on stream. A typical conversion-time curve is shown in Figure 1. The data presented in Tables I-IV are averages of several samples collected during a period, generally 2 hr, when the butadiene conversions were the highest.

Catalyst Deposits. At the relatively high temperature (500-550°C) used to disproportionate butadiene at high conversions, a high rate of coke laydown on the catalyst would normally be expected. As shown in Table I, the coke amounted to 1-2% of the converted butadiene; this is equivalent to a rate of coke deposition on the catalyst of 5-10% per hour.

Cyclohexene from Butadiene. Cyclohexadiene can be selectively hydrogenated to cyclohexene. This was demonstrated in a 10-hr cycle using a nickel-based selective hydrogenation catalyst. Conversion of cyclohexadiene and selectivity to cyclohexene were both near 100%. Combining disproportionation of butadiene to cyclohexadiene with selective hydrogenation of cyclohexadiene to cyclohexene provides a route for synthesizing cyclohexene from butadiene.

Summary

The postulated reaction paths for the synthesis of cyclohexene, cyclohexadiene, and benzene from butadiene are summarized in Figure 2. The relative yields of cyclohexadiene and of benzene are a function of process conditions. At high conversion levels (*i.e.*, >35%), the highest yield of cyclohexadiene obtained was at 515°C with catalyst containing 3% tungsten oxide, and the highest yield of aromatics was at 550°C with 16% tungsten oxide catalyst (Table V). Cyclohexadiene was hydrogenated at near 100% selectivity to cyclohexene.

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Received for review July 29, 1974
Accepted December 6, 1974

GENERAL ARTICLES

Catalytic Decomposition of Hydrogen Peroxide by Manganese–Alumina

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The potential of manganese–alumina for the catalytic decomposition of hydrogen peroxide was investigated in a continuous, tubular, packed bed reactor. First-order kinetics were suggested by the conversion time data. The effect of catalyst particle size on the apparent rate constants was shown to be highly significant. Tests on catalytic activity in the presence of ions such as citrate and phosphate indicated a severe inhibition. The catalytic ability of the manganese was shown to deactivate appreciably over a short time period and then stabilize. Immobilized catalases, in contrast, deactivate severely at identical substrate peroxide concentrations.

The catalytic decomposition of hydrogen peroxide is of interest in many areas of food processing. One suitable use of hydrogen peroxide is the sterilization of food products, for it destroys harmful organisms at low temperatures. Hence, hydrogen peroxide must be removed after its use in pasteurization of milk prior to cheese-making, (Rosell, 1961; Roundy, 1958) and after desugaring of egg whites (Scott, 1956). In addition, hydrogen peroxide occurs as a by-product which must be removed following the enzymatic production of gluconic acid, the enzymatic desugaring of eggs, and the enzymatic oxygen removal from fruit juices. In all these cases, an efficient method of decomposition of hydrogen peroxide into oxygen and water is required.

One method of hydrogen peroxide decomposition employs the enzyme catalase, either in the soluble form (Scott, 1956) or immobilized on a solid support (Traher and Kittrell, 1974). However, both beef liver catalase and, to a lesser degree, fungal catalase (Scott and Hammer, 1960) are rapidly inactivated by their substrate, hydrogen