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DEHYDROGENATION PROCESSES

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ABSTRACT OF THE DISCLOSURE

Hydrocarbons, such as alkylaromatic, alkanes alkenes, are dehydrogenated using a germanium dioxide catalyst with or without the presence of added oxygen.

The present invention relates to new processes for the dehydrogenation of chemical compounds and, in particular, relates to such processes carried out in the presence of a catalytic amount of germanium dioxide.

Conventional dehydrogenations, e.g. ethylbenzene to styrene, are generally accomplished at temperatures of from 600 to about 660° C. over catalysts, e.g. MgO, Fe_2O_3 or ZnO. These conventional processes usually encounter cracking and coking because of these relatively high temperatures. Because there is no oxidative effect, hydrogen is not removed from the reaction mixture by oxidation, and the conversion of ethylbenzene per pass is therefore equilibrium controlled. To obtain a favorable equilibrium, a large amount of steam is usually fed with the ethylbenzene to lower the partial pressure of styrene and hydrogen in the gas mixture. In such conventional processes, the catalyst is generally deactivated gradually with use and the reaction temperatures must be gradually raised to maintain economic levels of conversion.

The present invention in its preferred embodiments avoids the above disadvantages and permits the conversion of, for example, ethylbenzene to styrene, without the need for dilution with steam. Hydrogen is oxidatively removed as water, thus preventing the establishment of an equilibrium between ethylbenzene and styrene, and permitting good conversions of ethylbenzene to styrene.

The present invention is a process for dehydrogenation comprising the steps of contacting compounds which are capable of undergoing dehydrogenation with at least a catalytic amount of germanium dioxide at a temperature of preferably from about 300 to about 1,000° C. The reaction is preferably carried out in the vapor phase.

Temperatures of 500 to 800 will be more preferred and temperatures of 600 to about 750° C. are the most preferred range. Pressure is not narrowly critical but will preferably be from 0.1 to about 100 p.s.i.a. with pressures of from 7 to about 70 p.s.i.a. being most preferred. Contact times between the starting materials and the germanium dioxide are also not narrowly critical, but will preferably range from about 0.01 to about 1,000 seconds with contact times of 0.1 to about 10 seconds being most preferred.

Preheating of the starting materials to the above mentioned temperature ranges prior to contacting the germanium dioxide is highly desirable. Also desirable is the mixing of oxygen wtih the starting materials prior to the contacting of the germanium oxide. The preferred range of oxygen content of the feedstream is from 0.1 to about 100 with ranges of 0.5 to 50 being more preferred, and from about 0.5 to about 3 volumes of oxygen per volume of dehydrogenateable feed material being most preferred. Under almost all circumstances it will be important to avoid the explosive ranges of mixtures of O_2 with the feed materials. The oxygen may be supplied

in a non-interfering oxygen-containing gas, preferably air. The presence of a diluent such as nitrogen will, in some cases, permit the reaction to be carried out in otherwise explosive ranges without danger of explosion. The optimum ratios of oxygen, diluents and dehydrogenateable feed materials can readily be determined by routine trial runs.

The preferred dehydrogenateable feed materials for the process of the present invention are alkyl aromatics having from 1 to 3 alkyl groups with each alkyl group containing from 2 to about 6, more preferably 2 to about 3, and most preferably 2 carbon atoms; the preferred aromatic nuclei being benzene or naphthalene. Also among the preferred dehydrogenateable starting materials are alkanes, especially those having from 2 to about 10 carbon atoms (such as butane, isobutane, propane, and octane) and alkenes, especially those having from about 2 to about 10 carbon atoms and containing only a single double bond (such as butene-1, butene-2, hexene and octene).

The most preferred starting material for the present invention is ethylbenzene which dehydrogenates to form the valuable monomer, styrene, as discussed above.

The products of the present invention in general correspond to the feed materials, but contain additional double bonds. The preferred products of the present invention include: styrene, alpha-methylstyrene, butadiene, isoprene, vinylnaphthalene, and para-methyl styrene.

The germanium dioxide used in the present invention will preferably be present in catalytic amounts supported on a material such as silica, alumina or silicon carbide, or may be used in a pure state, preferably in the form of small pellets. The disposition of GeO_2 onto a support can be accomplished by treating the support material with $GeCl_4$ until the $GeCl_4$ is absorbed on the support and thereafter hydrolizing the $GeCl_4$ with water and then drying at temperatures of preferably about 200° C. or more in an inert atmosphere. The germanium dioxide will preferably be so arranged as to conveniently permit the preferred contact times mentioned above. Oxidation of the hydrogen formed by the dehydrogenation process will tend to deplete the germanium dioxide, but the GeO_2 will be continuously and automatically replenished where the above preferred amounts of oxygen are present in the feed stream.

The most preferred catalyst for the present invention is 1 to about 50 and especially 10 to about 25 weight percent GeO_2 based on the weight of the support which is preferably Carborundum (SiC).

The process of the present invention might, in some instances, be conducted on a batch basis. However, a flow basis will be very much preferred with the GeO_2 suspended in a suitable reactor chamber, e.g., a temperature and corrosion resistant tube and the feed stream being heated and caused to flow past the GeO_2.

The products of the present process can conveniently be separated in most instances by a series of partial condensers of successively lower temperatures, or by other conventional techniques.

The invention will be better understood by reference to the illustrative examples which follow. These are not to be taken as limiting the invention in any way and the claims appended hereto are to be considered as including the invention and all of its modifications and variations which will be apparent to persons skilled in the art.

Example 1

$GeCl_4$ 28 g., is adsorbed on 75 g. of 4–6 mesh porous Carborundum (CMM grade—Carborundum Company). The $GeCl_4$ is hydrolyzed with water and the catalyst dried at 250° C. in a stream of N_2.

Liquid ethylbenzene is fed to the reactor tube contain-

ing the catalyst at 5 cc./min. (all flow rates measured at room temperature), using a Kymograph syringe pump. The product is collected, separated from water and analyzed by gas-liquid chromatography. The results are given in Table 1.

TABLE 1.—DEHYDROGENATION OF ETHYLBENZENE ON A GeO_2-SiC CATALYST

Temp., ° C.	(370)	(485)	(540)
Ethylbenzene, percent	[1] 99.4	83.5	71.9
Styrene, percent	0.31	10.7	17.0
Toluene, percent		2.2	5.2
Benzene, percent	0.25	2.9	5.5
Other, percent		0.7	0.5

[1] Product analyses are wt. percent based on gas-liquid chromatography. Product analyses are conversions since no coking occurred.

Example II

The same as Example I, except the catalyst is prepared from 20 g. of $GeCl_4$ and 45 g. of silica gel. The results are shown in Table 2.

TABLE 2.—DEHYDROGENATION OF ETHYLBENZENE ON A GeO_2-SiO_2 CATALYST

	Temp., ° C.					
	(260)	(485)	(540)	(595) [1]		
				1st Pass	2d Pass	3d Pass
Ethylbenzene, percent	[2] 99.9	99.5	94.6	88.0	78.1	70.6
Styrene, percent	0.10	0.50	2.2	6.2	9.9	11.5
Toluene, percent	Trace	Trace	2.0	2.9	6.4	10.4
Benzene, percent	Trace	Trace	1.2	2.9	5.6	7.6
Other, percent						

[1] Total stream is recycled to determine the effect of longer residence times on the product distribution.
[2] Analyses are wt. percent based on gas-liquid chromatography. Product analyses are both conversions and selectivities since no coking occurs and no other liquid organic products are observed.

Example III

The experiments are done using 25 g. of pure GeO_2 tablets. In addition, a carrier gas (N_2) is used. The results are shown in Table 3.

TABLE 3.—DEHYDROGENATION OF ETHYLBENZENE OVER PURE GeO_2 IN A STREAM OF N_2 [1]

Temp., ° C.	(370)	(420)	(485)	(540)
Ethylbenzene, percent	[2] 98.5	98.2	86.9	87.3
Styrene, percent	1.0	1.4	7.9	8.5
Toluene, percent	0.5	0.4	5.2	1.9
Benzene, percent				

[1] N_2 flow 50 cc./min.
[2] Analyses are wt. percent based on gas-liquid chromatography. Product analyses are conversions since no coking occurs.

Example IV

Using the catalyst of Example III, a series of reactions are run in the presence of a small amount of oxygen. The results are shown in Table 4. The presence of oxygen resulted in better conversions of ethylbenzene to styrene.

TABLE 4.—DEHYDROGENATION OF ETHYLBENZENE OVER PURE GeO_2 IN A STREAM OF N_2 CONTAINING O_2 [1]

Temp., ° C.	(315)	(370)	(420)	(485)	(540)
Ethylbenzene, percent	[2] 96.8	96.9	92.2	85.7	63.4
Styrene, percent	2.8	2.3	5.5	10.7	24.9
Toluene, percent	0.4	0.3	0.3	0.7	5.2
Benzene, percent				2.3	6.4
Other, percent		0.5	20	0.4	

[1] N_2 flow 50 cc./min., O_2 flow 5 cc./min.
[2] Analyses are wt. percent based on gas-liquid chromatography. Product analyses are conversions since no coking occurs.

Example V

For comparison the catalyst of Example I and pure silicon carbide were used in reactions at 675° C., according to the procedures of Example I. The catalyst of Example I gave a 62 percent conversion of H_2 to water while pure silicon carbide gave only a 16 percent conversion of H_2 to water. This demonstrates the ability of GeO_2 to convert H_2 to water and facilitate oxidative dehydrogenation.

What is claimed is:

1. A dehydrogenation process comprising the steps of contacting organic compounds subject to dehydrogenation in the vapor phase with at least a catalytic amount of germanium dioxide at a temperature of from about 300 to about 1,000° C.

2. The production of aromatic compounds substituted with $CH{=}CH_2$ groups according to the process of claim **1** from alkyl aromatics containing from 1 to 3 alkyl groups with each alkyl group having from 2 to about 6 carbon atoms comprising in combination the steps of contacting said alkyl aromatics with at least a catalytic amount of germanium dioxide at a temperature of from 300 to about 1,000° C.

3. The process of claim **2** in which the alkyl aromatics are selected from the group consisting of alkyl benzenes and alkyl naphthalenes.

4. The process of claim **3** wherein said alkyl aromatics are vaporized and mixed with from 0.1 to about 100 moles of oxygen per mole of alkyl aromatic prior to contacting said germanium dioxide.

5. The process of claim **3** wherein the alkyl aromatic is an alkyl benzene.

6. The process of claim **3** wherein the alkyl aromatic is ethyl benzene.

7. The process of claim **1** wherein the compound subject to dehydrogenation comprises an alkane having from 2 to about 10 carbon atoms.

8. The process of claim **7** wherein the alkane is propane.

9. The process of claim **7** wherein the alkane is a butane.

10. The process of claim **7** wherein the alkane is pentane.

11. The process of claim **1** wherein the compound subject to dehydrogenation comprises an alkene having from about 2 to about 10 carbon atoms.

12. The process of claim **11** wherein the alkene is butene-1.

13. The process of claim **11** wherein the alkene is butene-2.

14. The process of claim **11** wherein the alkene is an isopentene.

No references cited.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

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It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 13, "alkylaromatic" should read -- alkylaromatics --. Column 3, TABLE 4, fourth column, line 4 thereof, "20" should read -- 2.0 --.

Signed and sealed this 3rd day of March 1970.

(SEAL)
Attest:

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