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HALOGENATED UNSATURATED HYDROCARBON PRODUCTION

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This invention relates to the production of halogenated unsaturated hydrocarbons. The invention relates more particularly to an improved process for the more efficient pyrolytic dehydrochlorination of alkyl chlorides to chlorinated unsaturated hydrocarbons. Still more particularly the invention relates to an improved process for the more efficient pyrolysis of ethylene dichloride to vinyl chloride.

Because of the highly endothermic nature of the reaction, the pyrolytic dehydrohalogenation of alkyl halides such as, for example, the pyrolytic dehydrochlorination of ethylene dichloride to vinyl chloride, must generally be effected in reaction zones having a restricted cross-sectional area. The use of tubular reactors as employed heretofore in such processes is, however, handicapped by difficulties deterring materially from their practical application. A serious difficulty heretofore often encountered is the relatively rapid deposition of solid, or high boiling, by-products which coke-up the tubes and limit the process to the utilization of only relatively short operating periods. The deposits formed are generally of such a nature that they require opening of the tubes and their removal therefrom by mechanical means. Execution of the reaction in unpacked reaction tubes often occasions the entrainment of high boiling reaction products from the reaction zone to an extent resulting in the fouling and clogging of parts of the apparatus such as heat exchangers, pumps, fractionators, and the like, through which the reaction products are passed. A still further difficulty often inherent in the use of unpacked tubular reactors is the inability to readily maintain a desired reaction temperature therein. The use of tubes having a relatively large diameter generally necessitates a reduction in throughput rates to an extent greatly accelerating carbon deposition and the formation of other desirable by-products. On the other hand, though the more rapid throughput rates which can be employed while still maintaining reaction temperatures in unpacked tubes of relatively small diameter reduces the rate of carbon deposition, the substantial restriction of cross-sectional area of such smaller tubes occasioned by even such lesser amounts of carbon deposition, generally results in a relatively rapid fouling and clogging.

The use of porous packing material such as, for example, clays, pumice, chamotte, charcoal, carbon, etc. may be resorted to aid in controlling the heat input into the reaction zone. The use

of such porous materials, it has been found, however, entails distinct disadvantages militating against efficient large scale operation of the process. The use of such porous packing material, although facilitating the control of the reaction temperature within the reaction zone, not only does not obviate the formation and deposition of carbonaceous deposits but generally materially aggravates these difficulties thereby increasing the rate at which fouling and clogging of the tubes is encountered. Though the carbonaceous deposit formed upon the porous packing material generally may be removed therefrom by the passage therethrough of oxygen-containing gases at relatively high temperatures, the frequency of the regenerative operation necessitated by the relatively rapid fouling of the porous packing materially increases to an inordinate degree the cost of the process. The considerable amount of carbonaceous deposit encountered when using a porous packing medium generally precludes the use of regeneration gases containing substantial amounts of oxygen. Not only is each regeneration period thereby considerably prolonged but readily available oxygen-containing gases, such as air can therefore not be employed. Because of the presence of hydrogen halide in the system, the restort to the use of steam to aid in effecting the regeneration of the porous packing material can generally not be desorted to. Its use results in a substantial increase in the corrosion rate of the metal surfaces of the apparatus unless these are made of certain costly alloys. As a consequence of such corrosion, metal oxides are deposited upon and retained by the porous support. During subsequent execution of the hydrohalogenation reaction the metal oxides are converted to metal halides which function as catalysts for the undesirable side reactions resulting in the formation of high boiling carbonaceous products thereby aggravating the difficulties due to fouling of the reactor and entrainment. A further disadvantage of such processes using porous packing material and thereby necessitating frequent drastic regenerations of the porous packing is the relatively rapid decrease in yield of the desired unsaturated alkyl halide as well as contamination of the product encountered therein. Liberation of oxygen by the metal oxides deposited upon the porous packing material results in the formation of oxygen-containing products such as carbon monoxide, carbon dioxide, etc. which contaminate the reaction product. The metallic halides formed in the porous packing further adversely affects the purity the unsaturated alkyl halide produced by catalyzing the decomposition of the alkyl halid charged with the formation of such undesirable product as acetylene olefines, and halogenated hydrocarbons other than the desired product.

A particular disadvantage of processes employing porous packing material in the reaction zone resides in the fact that the inherent difficulties, such as formation of carbonaceous deposit, product, contamination, reduction in yields, etc. become progressively more severe after each regeneration of the packing material. Thus in the production in vinyl chloride by the dehydrochlorination of ethylene dichloride in a reactor filled with a porous clay as packing material, the rate of formation of carbonaceous deposits and consequent fouling of the reactor was such as to necessitate regeneration of the packing material after each twenty-four hours of operation. After six such relatively short operating periods, each followed by a regeneration of the porous packing material, the crude vinyl chloride obtained contained only 89% vinyl chloride and the following indicated amounts of impurities:

	Weight per cent
CO	0.4
CO_2	0.6
Acetylene	1
Ethylene	5.8
Methane and ethane	0.2
Dichloroethane	3

Since the suitability of the vinyl chloride product as a starting or intermediate material in many processes is often dependent upon a relatively high degree of purity, its production in processes utilizing porous packing material in the reaction zone would of necessity entail the discarding of the packing material after an operation of only relatively short duration, or the resort to additional complex and costly purifying steps.

It is an object of the present invention to provide an improved process enabling the more efficient production of unsaturated halogenated hydrocarbons. Another object of the invention is the provision of an improved process enabling the more efficient pyrolysis of alkyl chlorides to chlorinated unsaturated hydrocarbons. A particular object of the invention is the provision of an improved process enabling the more efficient pyrolysis of ethylene dichloride to vinyl chloride. Other objects and advantages of the invention will become apparent from the following detailed description thereof.

It has now been found that the difficulties heretofore encountered in the production of halogenated unsatuated hydrocarbons by the pyrolytic dehydrohalogenation of alkyl halides are obviated to at least a substantial degree and the objects and advantages of the invention obtained, by executing the dehydrohalogenation of the alkyl halide in a reaction zone containing a non-catalytic non-porous packing material. In accordance with the process of the invention an alkyl halide is passed in the vapor phase, at pyrolytic dehydrohalogenating conditions, through an externally heated reaction zone containing a non-porous packing material, thereby converting the alkyl halide to reaction products consisting essentially of a halogenated unsaturated hydrocarbon and hydrogen halide in the absence of any substantial formation of by-products and of any substantial deposition of carbonaceous material within the reaction zone.

Suitable non-porous packing materials employed in the process of the invention comprise any of the available non-porous or smooth-surfaced, thermally stable packing materials which are inert under the conditions of execution of the reaction. The non-porous packing material employed may be of natural or synthetic origin. Examples of the broad class of suitable non-porous packing materials substantially devoid of micropores are the non-metallic, smooth-surfaced or non-porous, naturally occurring stony materials as, for example, gravel, pebbles, crushed rock, granite, and the like; manufactued smooth-surfaced, or non-porous, materials such as granules, particles, fragments, chunks, pieces, or the like of ceramic material, glass, porcelain, etc.; examples of such manufactured non-porous packing materials are Raschig rings, porcelain tubes, porcelain saddles, porcelain disks, glass marbles, rock wool, glass wool, glass beads, and the like. A particularly desirable and preferred non-porous packing material comprises pebbles, or gravel. The size of the individual pieces, fragments, chunks, or the like, of non-porous packing material may vary widely within the scope of the invention. A particularly suitable non-porous packing material for use in reaction zones of restricted cross-sectional areas are pebbles, or gravel, having a particle size of from about 1 to about 3 cm.

The process of the invention is applied broadly to the pyrolytic dehydrohalogenation of alkyl halides containing at least two halogen atoms in the molecule to a corresponding halogenated unsaturated hydrocarbon. The halogen substituent of the alkyl halide charged may consist, for example, of chlorine, bromine or iodide. The process of the invention lends itself with advantage to the treatment of the di- and tri-halo-substituted hydrocarbons. Examples of alkyl halides pyrolytically dehydrohalogenated in accordance with the process of the invention are 1,1-dichloroethane, 1,2-dichloroethane, trichloroethanes, dichloropropanes, trichloropropanes, dichlorobutanes, trichlorobutanes, dibromoethanes, dibromopropanes, tribromopropanes, dibromobutanes, tribromobutanes, and higher boiling saturated alkyl chlorides and bromides having at least two halogen atoms in the molecule.

The charge to the system need not necessarily consist of a single alkyl halide but may comprise two or more alkyl halides. Gaseous materials, inert under the conditions of execution of the reaction, such as, for example, nitrogen, may be introduced into the system together with the charge or may be introduced in part or entirety into the reaction zone at a plurality of spaced points along the length thereof.

The reaction zone may comprise a reaction chamber or a tubular reactor, or a plurality of such chambers or tubular reactors arranged in series or in parallel with one another, provided with means for maintaining the dehydrohalogenating conditions of temperature therein and for containing the non-porous packing. A particularly preferred type of reactor comprises an externally heated reaction zone of restricted cross-sectional area such as, for example, reaction tubes or coils positioned in a suitable furnace structure. Other suitable types of reactors comprise furnace-type structures containing one or more beds of non-porous packing material, means for the passage of the alkyl halide charge through said bed or beds, and means for maintaining said beds at pyrolytic dehydrohalogenating temperatures.

The alkyl halide charge to the system such as, for example, ethylene dichloride is passed into the reaction zone through an inlet positioned at one end thereof, or may be introduced in part through such inlet and the remainder through a plurality of inlets spaced along the length of said reaction zone. The reaction zone is maintained at a sufficiently high temperature to effect the dehydrohalogenation of the alkyl halide charged with the formation of reaction products consisting essentially of the corresponding halogenated unsaturated hydrocarbon and halogen halide. Thus, in the pyrolysis of ethylene dichloride to vinyl chloride the reaction zone is maintained at a temperature of from about 425° C. to about 675° C., and preferably from about 475° C. to about 625° C. Subatmospheric, atmospheric, or superatmospheric pressures may be maintained within the reaction zone. Suitable pressures comprise the pressures in the range of from substantially about 1 to about 10 atmospheres. Higher or lower pressures may, however, be employed within the scope of the invention.

Under the above-defined conditions ethylene dichloride is converted to reaction products consisting of vinyl chloride and hydrogen chloride in the reaction zone.

Effluence from the reaction zone comprising unsaturated alkyl halide, hydrogen halide and unconverted alkyl halide is passed to suitable separating means to effect the separation of unsaturated alkyl halide therein. Unconverted alkyl halide separated from the reaction products is preferably recycled to the reaction zone, optionally after separating therefrom any higher boiling reaction products which may have been formed in the process.

Any carbon or carbonaceous products deposited upon the non-porous support after a prolonged period of operation are readily removed therefrom by the passage of an oxygen containing gas such as, for example, air, flue gas, etc. therethrough at a reaction zone temperature of, for example, from about 500° C. to about 700° C.

Execution of the pyrolytic dehydrohalogenation in the presence of non-porous packing material, it has been found, not only enables the attainment of such significant advantages as substantially increased lengths of operating periods before regeneration of the packing material is required, substantial reduction in the rate of carbon deposition, and elimination to at least a substantial degree of the difficulties due to entrainment and clogging of the apparatus, but often makes possible the attainment of these advantages together with a substantial increase in the yield of the desired halogenated unsaturated hydrocarbon. A further significant advantage inherent in the use of non-porous packing material resides in the ability to effect the removal of the lesser amount of carbonaceous deposits efficiently and in exceedingly short time in situ with gaseous media having a relatively high oxygen content, thereby enabling resort to the economically advantageous expedient of utilizing air as the regenerating medium. The non-porous packing material possesses the still further advantage of being able to be regenerated, even after relatively long periods of operation, without suffering the adverse effects peculiar to porous materials which upon regeneration progressively increase the initial difficulties at an inordinately rapid rate. The substantial improvement obtained in the production of vinyl chloride by the pyrolytic dehydrochlorination of ethylene dichloride in accordance with the process of the invention utilizing a reaction zone packed with non-porous packing material as compared with processes employing reactors containing no packing, or containing packing of a porous character, is evidenced by the following examples:

EXAMPLE I

In twelve separate operations ethylene dichloride was dehydrohalogenated to vinyl chloride and hydrogen chloride by passage through an externally heated, stainless steel, tubular reactor at a pressure of 100 lbs. The charge was passed through the reactor at the rate of 62 lbs. of ethylene dichloride per hour in all of the operations except in runs 2 and 3 wherein the throughput rate was reduced to 42 lbs. and 27 lbs., respectively, in an effort to increase the conversion. The packing employed in the reactor, reaction temperature, total ethylene dichloride conversion, duration of the run, and the reason for stopping the run are indicated in the following table for each individual operation.

Table I

Run	Packing	Temperature, ° C.	Conversion, Per Cent	Duration, Hours	Remarks
1	None	600	49	58.5	Reactor Plugged.
2	None	600	84	51	Do.
3	None	600	52	61	Do.
4	4/6 Mesh Carborundum	600		4	Do.
5	do	550	67	11	Do.
6	Pelleted Diatomaceous Earth (Celite VIII).	600		1	Do.
7	½ in. Carbon Rings	600	75	26	Do.
8	Pumice	600		8	Reactor Exit Restricted.
9	0.3/0.4 in. Gravel	550	63	114	Separator Adjustment.
10	do	550	56.2	127	Reactor Plugged.[1]
11	Regenerated Gravel from Run 10	550	39	107	Separator Adjustment.

[1] The last part of run 10 was carried out with recycling of unconverted and high boiling materials resulting in a drop of conversion to 30.3%. An inhibitory action by traces of high boiling material in the recycle stream is strongly suggested. It is estimated that without such recycle, or by removing the traces of high boiling material from the recycle stream by fractionation or other means, the run could have been extended over 170 hours.

It is immediately apparent from the foregoing example that the period of operation is considerably increased by the utilization in the reaction zone of a non-porous packing material. It is to be noted that runs 9 and 11 were terminated long before any substantial clogging of the reactor or fouling of the packing material was encountered. The gravel packing employed in run 10 was regenerated by passage of air through the reactor of a temperature of 600° C. until substantially all carbonaceous deposit was removed therefrom. The highly advantageous nature of the non-porous packing is further evidenced by the long period of operation attained in run 11 with the thus regenerated packing. Run 11 is to be noted, was also terminated prior to any indication of clogging of the reactor. The gravel packing from run 11 was again regenerated and employed in a total of 60 additional hours of operation.

It is also seen from the foregoing example that, though the presence of a porous packing material in the reactor results in a substantial increase in the conversions over those obtained with empty tubes, such increase is, however, obtained at the cost of a reduction of the period of operation substantially below that commensurate with practical operation of the process. The inordinate increase in the rate of carbon deposition occasioned by the presence of the porous support and the extent to which a non-porous packing material reduces its formation is illustrated by the following example:

EXAMPLE II

Ethylene dichloride was dehydrochlorinated to vinyl chloride in four separate and independent operations (runs 1 to 4) by passage through an externally heated unpacked tubular reactor. In two additional operations (runs 5 and 6) ethylene dichloride was dehydrochlorinated by passage through a tubular reactor packed with pumice and gravel, respectively. After each run the tubes were opened and the carbon deposition determined. The temperature of operation, duration of the run in hours, and the amount of carbon deposition in pounds per 100 pounds of feed is indicated for each run in the following table:

Table II

Run	Packing	Reaction Temperature, ° C.	Duration of Run, Hours	Carbon Deposition, lbs./100 lbs. feed
1	None	600	4	0.056
2	None	600	4	0.059
3	None	664	19.8	0.04
4	None	606	51.3	0.02
5	Pumice	600	8	0.24
6	0.3/0.4 in. Gravel	550	114	0.025

It is seen that the packing of the reactor with pumice resulted in carbon deposition equal to about four times the highest value obtained with an unpacked reactor. When using gravel as packing material, on the other hand, the reactor was found to be remarkably clean and the gravel packing to be coated with only a microscopic film after 114 hours of continuous operation.

The signal advantages of the process of the invention attributable to the use of non-porous packing in the reaction zone furthermore comprise the ability to attain excellent yields of the desired vinyl chloride, often exceeding those attainable with the use of a porous packing material under otherwise identical operating conditions. The substantial increase in yields obtainable over longer periods of operation, not only with fresh non-porous packing but with non-porous packing which has been used in previous operations and subjected to repeated regenerations is illustrated by the following example:

EXAMPLE III

In a plurality of separate operations ethylene dichloride was dehydrochlorinated to vinyl chloride and hydrogen chloride by passage through an externally heated tubular reactor at a pressure of 2 atm. abs. and a throughput rate of 0.78 kg. of ethylene dichloride per liter of packing material per hour. The tubular reactor was heated by immersion in a molten salt bath maintained at 500 to 570° C.

In one series of operations the tubular reactor was packed with a porous fire clay of 10 to 15 mm. grain size. After each run the packing was regenerated by passage therethrough of an oxygen-containing stream at a temperature of about 500° C. and at the rate of 3000 liters of oxygen-containing gas per hour. The thus regenerated packing was then employed in the subsequent run. The yield of vinyl chloride obtained in mole per cent of the theoretical yield and the length of operation for each run are indicated in column A of the following Table III.

Ethylene dichloride was dehydrochlorinated in a separate series of operation under substantially identical conditions with the exception that the tubular reactor was packed with porous gravel of 15 to 2 mm. particle size. The yield of vinyl chloride obtained in mole per cent of theoretical yield and the duration of the operation for each run are indicated in column B of the following Table III.

Table III

Run	Packing	A Clay		B Gravel	
		Yield	Duration, Hours	Yield	Duration, Hours
1A	Fresh Packing	86	24	95.5	36
1B	Regenerated from 1A.	86	24	94.0	24
1C	Regenerated from 1B.	88	24	94.7	48
1D	Regenerated from 1C.	86	33	94.2	93

A particular advantage of the invention attributable to the use of non-porous packing material is the elimination of the need for the use of reactors constructed of relatively costly alloy materials. Thus the process may be executed in iron or ferrous metal reactors without substantial contamination of the crude vinyl chloride product, even after repeated regenerations of the packing material. This is attributable, as indicated above, to the absence for the need of steam to temper the regeneration and the absence of any excessive temperature rise during regenerations due to the low rate of carbon deposition, which obviate to at least a substantial degree the corrosion of reactor walls and the deposition upon the packing of metal compounds conducive to product contamination. Whereas the crude vinyl chloride product obtained in run 1A of Example III after only 24 hours of operation with a fresh porous packing contained 97.1% by weight of vinyl chloride, the crude vinyl chloride product obtained from run 1C employing the non-porous packing material used for 108 hours of total operation and which had been subjected to two regeneration operations still contained 98.4% vinyl chloride.

Although the illustrative examples have stressed the application of the invention to the dehydrochlorination of ethylene dichloride (1,2-dichloroethane) the process is applied with advantage to the dehydrohalogenation of other halogenated hydrocarbons as exemplified by the following example:

EXAMPLE IV

A dichloroethane charge consisting of 90% 1,1-dichloroethane and 10% 1,2-dichloroethane was passed through a 3.07 in. I. D. externally heated stainless steel tubular reactor of 0.45 cu. ft. capacity at 550 C., a pressure of 100 lbs. gauge and a throughput rate of 50 lbs. of dichloroethane charge per hour. The tubular reactor was packed with non-porous gravel of 0.3 to 0.4 in. particle size. The operation was terminated after 20 hours of continuous operation. A conversion of 35% and a yield of vinyl chloride of 98.2 mol per cent was obtained.

The invention claimed is:

1. The process for the production of vinyl chloride which comprises passing ethylene dichloride in the vapor phase at a temperature of from about 425° C. to 675° C. through a bed of inert gravel consisting of smooth surfaced rounded fragments of rock positioned in a reaction zone of restricted cross-sectional area.

2. The process for the production of vinyl chloride which comprises passing ethylene dichloride in the vapor phase at a temperature of from about 425° C. to about 675° C. through a bed of inert gravel consisting of smooth surfaced rounded fragments of rock ranging in size from about 1 to about 3 cm. in diameter positioned in a reaction zone of restricted cross-sectional area.

3. The process for the production of vinyl chloride which comprises passing ethylene dichloride in the vapor phase at a temperature of from about 425° C. to about 675° C. through a bed of inert smooth surfaced pebble gravel positioned in a reaction zone of restricted cross-sectional area.

4. The process for the production of vinyl chloride which comprises passing 1,1-dichloroethane in the vapor phase at a temperature of from about 425° C. to about 675° C. through a bed of inert gravel consisting of smooth surfaced rounded fragments of rock positioned in a reaction zone of restricted cross-sectional area.

5. The process for the production of vinyl chloride which comprises passing dichloroethane in the vapor phase at a temperature of from about 425° C. to about 675° C. through a bed of inert gravel consisting of smooth surfaced rounded fragments of rock positioned in a reaction zone of restricted cross-sectional area.

6. The process for the production of vinyl halide which comprises passing dihaloethane in the vapor phase at a temperature of from about 425° C. to about 675° C. through a bed of inert gravel consisting of smooth surfaced rounded fragments of rock positioned in a reaction zone of restricted cross-sectional area.

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