

Description

This invention relates to a process for converting toluene and butadiene to styrene and 1-pentene.

Butadiene is a commodity chemical, which, because of economic cycles, can be at times in surplus. When it is in surplus, it is desirable to convert it to higher value products. Styrene is a valued chemical which finds many uses, such as being used as a component in styrenic polymers. Coproduct 1-pentene can be used as a feedstock to prepare specialty detergents or lube stocks.

In Applied Industrial Catalysis, Vol. 3, Ed. B. C. Leach, Acad. Press 1984, Chapter 7 (pages 215-239) "Olefin Metathesis: Technology and Application" by R. L. Banks discloses in pages 233-244 a method for the production of styrene, wherein toluene is first converted to stilbene over lead oxide, followed by cleavage of the stilbene with ethylene over a base-treated tungsten oxide-silica metathesis catalyst. More generally about processes of olefin metathesis or disproportionation, the same chapter discloses in pages 218-219 that the more effective catalysts are the oxides of molybdenum, tungsten and rhenium supported on high-surface area alumina or silica, and in pages 221-222 that these processes operate over wide ranges of temperature, pressure, space rate and cycle length, depending on the catalyst system and specific application.

The instant invention relates to a process for converting toluene and butadiene to styrene and 1-pentene, which process comprises:

- a) reacting toluene and 1,3-butadiene in the presence of an alkali metal catalyst,
- b) contacting the reaction product of step a) with a double bond isomerization catalyst,
- c) reacting the isomerized product of step b) with ethylene in the presence of a disproportionation catalyst, and
- d) separating styrene and 1-pentene from the product of step c).

The first step of the instant process is to react toluene with 1,3-butadiene in the presence of a metallic alkali metal catalyst. While any of the Group IA metals can be utilized as a catalyst, sodium and potassium are preferred. The alkali metal catalyst can be utilized as such in a dispersed form in the reaction medium or, preferably, it is supported on a nonacidic oxide support. Group IA and Group IIA oxides are typically utilized as supports and preferably calcium oxide and sodium oxide are utilized. Alumina also provides a suitable support. Mixed metallic alkali metals can be utilized, such as a sodium-potassium mixture supported on calcium oxide.

The butenylation reaction is carried out at temperatures ranging from 0°C to 150°C and preferably from 25°C to 130°C. Reaction pressures are not critical and will typically range from atmospheric pres-

sure to 100 bars.

The butenylation reaction may be carried out in a batch reactor or in a continuous flow reactor. For example, it may be carried out in a traditional fixed bed reactor, the bed comprising a supported metallic alkali metal catalyst, wherein toluene and butadiene in a cocurrent or counter current flow mode is passed over the bed to carry out the reaction. Trickle phase and continuous stirred tank reactors are also suitable. Other continuous reactor configurations will be readily apparent to one skilled in the art.

Batch reactors, such as autoclaves, are also suitable. For example, reactant toluene and catalyst are charged to an autoclave which is then pressured with butadiene and heated to the reaction temperature to allow the reaction to be carried out. Alternatively, reactant toluene and catalyst are charged to a stirred tank reactor and butadiene is bubbled through the reaction at reaction temperature in order to carry out the reaction.

To avoid multiple butenylated products the molar ratio of reactant toluene to butadiene is kept at greater than one. Batch reactions utilizing an excess of toluene in conjunction with a controlled addition of the butadiene yield a monobutenylated product exclusively.

After reaction is complete, the reaction mixture can be treated to remove any remaining catalyst by well known means, such as filtration, with or without decomposition of the catalyst, flash distillation, etc. At this point, butenylated reaction product can be separated from the reaction mixture by traditional means such as distillation or fractional crystallization and the butenylated toluene passed on to the second, or isomerization step of the instant process. Alternatively, the reaction mixture can be flashed to remove unreacted butadiene, and the resulting product passed on to the isomerization step.

The major product of the butenylation reaction will be 5-phenyl-2-pentene.

The second step of the instant process comprises isomerizing the butenylated reaction product of the first step by contact with a double bond isomerization catalyst at isomerization conditions. The double bond isomerization catalysts that are employed in the second step are any of the well known isomerization catalysts which promote double bond isomerization with little or no concurrent polymerization or cracking. Suitable examples are exemplified as phosphoric acid, both supported and unsupported, bauxite, alumina supported cobalt oxide, or iron oxide or manganese oxide, alkali metals such as sodium and potassium on an inert carrier materials such as alumina, alkali metal promoted aluminas such potassium carbonate on alumina, supported platinum group metals, magnesium oxide, calcium oxide, metal hydrides, organoalkali compounds, metal hydroxides and the like. Other suitable isomerization catalysts are disclosed

in the publications "Review of Olefin Isomerization", H.N. Dunning, Industrial and Engineering Chemistry, 45, 551-564 (1953) and "Base-Catalyzed Reactions of Hydrocarbons and Related Compounds", edited by H. Pines and W.M. Stalich, Academic Press, 1977, pp.25-51. Particularly suitable catalysts are the alkali metal carbonate promoted aluminas, such as those prepared by impregnating a porous alumina support with a solution of an alkali metal carbonate, such as potassium carbonate, drying and calcining under a flow of nitrogen at elevated temperatures, say, 575°C for fourteen hours.

The isomerization reaction is carried out temperatures ranging from 50°C to 200°C, preferably from 75°C to 175°C, and more preferably from 100°C to 150°C. Reaction pressures are not critical and will typically range from atmospheric pressure to 100 bars.

The isomerization reaction may be carried out in a batch reactor or in a continuous flow reactor. For example, it may be carried out in a traditional fixed bed reactor, the bed comprising a supported metallic alkali metal catalyst, wherein the butenylated product from the first reaction is passed over the bed to carry out the reaction. Trickle phase and continuous stirred tank reactors are also suitable. Other continuous reactor configurations will be readily apparent to one skilled in the art.

Batch reactors, such as autoclaves, are also suitable. For example, the butenylated product reactant toluene and catalyst are charged to an autoclave which is then heated to the reaction temperature to allow the isomerization reaction to be carried out.

After the isomerization reaction is complete, the reaction mixture can be treated to remove any remaining catalyst by well known means, such as filtration, with or without decomposition of the catalyst, flash distillation, etc. At this point, the isomerized reaction product can be separated from the reaction mixture by traditional means such as distillation or fractional crystallization and passed on to the third or ethenolysis step of the instant process. Non-isomerized 5-phenyl-2-pentene can be recycled to the isomerization step.

The major product of the isomerization reaction will be 1-phenyl-1-pentene.

The third step of the instant process comprises reacting the isomerized reaction product of the second step with ethylene in the presence of a disproportionation catalyst. The disproportionation catalysts employed in the third step of the instant process are also known in the prior art. Any solid catalyst system which is capable of promoting or catalyzing the olefin disproportionation reaction of butene-2 and ethylene to propylene is suitable. Preferably the disproportionation catalyst is one of molybdenum, tungsten and/or rhenium oxide supported on a refractory oxide support, preferably alumina. In particular, a catalyst com-

prising rhenium oxide, supported on alumina is preferred. These solid catalysts can also contain minor amounts of various treating agents, such as trialkylaluminum compounds, dialkylaluminum halides, mono- and polyvalent alcohols, and the like. It is also sometimes advantageous to treat the solid catalyst with suitable gases, such as carbon dioxide, hydrogen and the like. The disproportionation catalysts can also be treated with the alkaline earth and alkali metal compounds as reported in the prior art. Preferably, a compound of sodium or potassium is used. Rhenium catalysts have also been promoted with tin compounds, such as tin oxide. Tetraalkyl tin compounds have also been utilized as promoters. The tetraalkyl tin compounds (alkyl being lower alkyl of C₁-C₃) are added to the reaction mixture to increase the activity of the rhenium catalyst. Tetramethyl tin, tetraethyl tin, tetrapropyl tin and tetrabutyl tin compounds are frequently utilized. An alumina supported rhenium catalyst promoted by tetraalkyl tin, preferably tetrabutyl tin, is a preferred catalyst for the ethenolysis reaction.

The ethenolysis reaction is carried out at temperatures ranging from -10°C to 100°C, preferably from 0°C to 80°C, more preferably from 20°C to 50°C. Reaction pressures are not critical and will typically range from atmospheric pressure to 100 bars.

The ethenolysis reaction may be carried out in a batch reactor or in a continuous flow reactor. For example, it may be carried out in a traditional fixed bed reactor, the bed comprising the supported disproportionation catalyst, wherein the isomerized product from the isomerization reaction and ethylene in a co-current or counter current flow mode is passed over the bed to carry out the reaction. Trickle phase and continuous stirred tank reactors are also suitable. Other continuous reactor configurations will be readily apparent to one skilled in the art.

Batch reactors, such as autoclaves, are also suitable. For example, isomerized product from the isomerization reaction and catalyst are charged to an autoclave which is then pressured with ethylene and heated to the reaction temperature to allow the reaction to be carried out. Alternatively, isomerized product from the isomerization reaction and catalyst are charged to a stirred tank reactor and ethylene is bubbled through the reaction at reaction temperature in order to carry out the reaction.

After reaction is complete, the reaction mixture can be treated to remove any remaining catalyst by well known means, such as filtration or centrifugation. At this point styrene and 1-pentene can be separated from the reaction mixture by traditional means. For example, flash distillation can be used to remove the 1-pentene and ethylene, followed by further distillation to separate pentene and ethylene, and fractional distillation can be used separate out the styrene.

Inert solvents such as alkanes, e.g., cyclohex-

ane, dodecane, hexadecane, octane, nonane, etc., can be utilized in either or all of the butenylation, isomerization or ethenolysis steps.

The invention will be described by the following example which is provided for illustrative purposes and is not to be construed as limiting the invention.

Example

A. Butenylation Reaction

Catalyst Preparation:

Finely powdered calcium oxide was heated in a quartz tube to 575°C under a flow of dry nitrogen (200ml/min). The freshly calcined calcium oxide (50g) was placed in a 500ml single neck Morton flask with 1.5 g of sodium metal chips under a nitrogen atmosphere. The mixture was heated to about 200-240°C and tumbled on a rotary evaporator for 3 hours under an argon atmosphere to give a uniform grey-purple powder.

Reaction:

The freshly prepared sodium on calcium oxide catalyst (50g) was placed under a nitrogen atmosphere in a 500ml three necked flask equipped with an air stirrer, reflux condenser, thermometer, gas inlet tube for the introduction of nitrogen and 1,3-butadiene and a gas outlet tube. Dry toluene (185g, 2.0 mole) was added to the catalyst and the mixture was stirred and heated to 90-95°C under a nitrogen blanket. Butadiene (49g, 0.91 mole) was bubbled through the stirred mixture over a period of 7 hours at 90-95°C.

The reaction mixture was cooled to 20°C and the catalyst was destroyed by the slow addition of isopropyl alcohol. The reaction mixture was filtered through a celite pad and the solids were washed with toluene. The toluene wash and filtrates were combined and washed with deionized water until neutral and then dried over magnesium sulfate. Filtration followed by distillation via a 15 cm vigeroux column yielded 28.3 g (10% yield based on conversion of toluene and 22% yield based on conversion of butadiene) of a colorless oil (b.p. 199-21°C). Analysis by gas chromatography, GC/MS and ¹³C NMR showed the product to be 94% 5-phenyl-2-pentene (mixture of cis and trans isomers), 4% 5-phenyl-1-pentene and less than 1% 1-phenyl-1-pentene.

B. Isomerization Reaction:

Catalyst:

The catalyst was a 15%K₂CO₃/alumina which was prepared by impregnating alumina (Kaiser KA-

201 alumina) with a aqueous potassium carbonate solution, drying and calcining at 120°C for 14 hours, followed by activation in nitrogen at 575°C for 14 hours.

Reaction:

A 100 ml stirred Parr autoclave was charged with a nitrogen purged solution of 29.0 grams of 5-phenyl-2-pentene from the above butenylation reaction in 35 ml of dry hexadecane and 10 grams of activated 15%K₂CO₃/alumina. The autoclave was sealed, stirred at 120-130°C for 5.5 hours, cooled to 20°C and the catalyst was filtered off. Analysis of the filtrate by GC/MS and ¹³C NMR showed the product to be 63% 1-phenyl-1-pentene (68% isomerization), 30% 5-phenyl-2-pentene and 1% 5-phenyl-1-pentene.

C. Ethenolysis Reaction:

Catalyst:

The catalyst was a 15%Re₂O₇/alumina material which had been activated by heating at 540°C for 2.5 hours under an air flow of 20 l/h followed by heating at 540°C under a nitrogen flow of 20 l/h for 1.5 hours.

Reaction:

To a nitrogen-purged 100ml Hoke addition vessel was added a nitrogen purged solution of about 28 grams of the product mixture of the isomerization step containing 63% 1-phenyl-1-pentene and 30% 5-phenyl-2-pentene, 35 ml of dry nitrogen-purged hexadecane and 1.6 ml (5 mmole) of tetrabutyl tin under a nitrogen atmosphere. To a 100 ml Parr autoclave, under a nitrogen atmosphere, was added 6.0g (5 mmole of rhenium) of the activated rhenium oxide/alumina catalyst. The hoke addition vessel was affixed to the Parr autoclave and the contents of the Hoke vessel were pressured into the autoclave with 35 bar of ethylene at room temperature. The reaction mixture was stirred for 16 hours under 35 bar ethylene pressure, cooled to 5°C and then the gas pressure was vented off through a gas sample vessel. Analysis of gas sample by GC/MS verified that the only two significant ethenolysis products obtained were propylene (from ethenolysis of 5-phenyl-2-pentene) and 1-pentene (from ethenolysis of 1-phenyl-1-pentene). Propylene could have been eliminated had the non-isomerized 5-phenyl-2-pentene been separated out prior to ethenolysis. Analysis of the liquid fraction of the reaction mixture by GS/MS, gas chromatography and ¹³C NMR established a 95% conversion of the 1-phenyl-1-pentene to styrene.

Claims

1. A process for converting toluene and butadiene to styrene and 1-pentene, which process comprises:
 - a) reacting toluene and 1,3-butadiene in the presence of an alkali metal catalyst,
 - b) contacting the reaction product of step a) with a double bond isomerization catalyst,
 - c) reacting the isomerized product of step b) with ethylene in the presence of a disproportionation catalyst, and
 - d) separating styrene and 1-pentene from the product of step c).
2. A process as claimed in claim 1 wherein step a) is carried out at a temperature ranging from 0°C to 150°C, step b) is carried out at a temperature ranging from 50°C to 200°C and step c) is carried out at a temperature ranging from -10°C to 100°C.
3. A process as claimed in claim 2 wherein step a) is carried out at a temperature ranging from 25°C to 130°C, step b) is carried out at a temperature ranging from 75°C to 175°C and step c) is carried out at a temperature ranging from 0°C to 80°C.
4. A process as claimed in any one of claims 1-3 wherein the alkali metal catalyst comprises sodium or potassium deposited on calcium oxide or aluminum oxide, the isomerization catalyst comprises a porous alumina promoted by potassium carbonate and the disproportionation catalyst comprises rhenium oxide supported on alumina
5. A process as claimed in claim 4 wherein the disproportionation catalyst is promoted with tetraalkyl tin.
6. A process as claimed in claim 5 wherein the tetraalkyl tin is selected from tetramethyl tin, tetraethyl tin, tetrapropyl tin, tetrabutyl tin and mixtures thereof.

Patentansprüche

1. Ein Verfahren zur Umwandlung von Toluol und Butadien in Styrol und 1-Penten, welches Verfahren die folgenden Verfahrensschritte umfaßt:
 - a) Umsetzen von Toluol und 1,3-Butadien in Gegenwart eines Alkalimetallkatalysators,
 - b) Kontaktieren des Reaktionsprodukts von Stufe a) mit einem Doppelbindungs-Isomerisierungskatalysator,
 - c) Umsetzen des isomerisierten Produkts von Stufe b) mit Ethylen in Gegenwart eines Dis-

proportionierungskatalysators, und
d) Abtrennen von Styrol und 1-Penten aus dem Produkt von Stufe c).

2. Ein Verfahren, wie in Anspruch 1 beansprucht, in welchem Stufe a) bei einer Temperatur im Bereich von 0°C bis 150°C, Stufe b) bei einer Temperatur im Bereich von 50°C bis 200°C und Stufe c) bei einer Temperatur im Bereich von -10°C bis 100°C durchgeführt werden.
3. Ein Verfahren, wie in Anspruch 2 beansprucht, in welchem Stufe a) bei einer Temperatur im Bereich von 25°C bis 130°C, Stufe b) bei einer Temperatur im Bereich von 75°C bis 175°C und Stufe c) bei einer Temperatur im Bereich von 0°C bis 80°C durchgeführt werden.
4. Ein Verfahren, wie in einem der Ansprüche 1 bis 3 beansprucht, in welchem der Alkalimetallkatalysator Natrium oder Kalium auf Calciumoxid oder Aluminiumoxid enthält, der Isomerisierungskatalysator ein poröses Aluminiumoxid mit Kaliumcarbonat als Promotor enthält und der Disproportionierungskatalysator Rheniumoxid auf Aluminiumoxid als Träger enthält.
5. Ein Verfahren, wie in Anspruch 4 beansprucht, in welchem der Disproportionierungskatalysator Tetraalkylzinn als Promotor enthält.
6. Ein Verfahren, wie in Anspruch 5 beansprucht, in welchem das Tetraalkylzinn ausgewählt ist aus Tetramethylzinn, Tetraethylzinn, Tetrapropylzinn, Tetrabutylzinn und Mischungen davon.

Revendications

1. Un procédé pour la conversion de toluène et de butadiène en styrène et en pentène-1, qui comprend :
 - a) la réaction de toluène et de butadiène-1,3 en présence d'un catalyseur à base de métal alcalin,
 - b) la mise en contact du produit de réaction de l'étape a) avec un catalyseur d'isomérisation des doubles liaisons,
 - c) la réaction du produit isomérisé de l'étape b) avec l'éthylène en présence d'un catalyseur de dismutation, et
 - d) la séparation du styrène et du pentène-1 du produit de l'étape c).
2. Un procédé selon la revendication 1, dans lequel l'étape a) est conduite à une température comprise entre 0°C et 150°C, l'étape b) est conduite à une température comprise entre 50°C et 200°C



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et l'étape c) est conduite à une température comprise entre -10°C et 100°C.

3. Un procédé selon la revendication 2, dans lequel l'étape a) est conduite à une température comprise entre 25°C et 130°C, l'étape b) est conduite à une température comprise entre 75°C et 175°C et l'étape c) est conduite à une température comprise entre 0°C et 80°C. 5 10
4. Un procédé selon l'une quelconque des revendications 1-3, dans lequel le catalyseur à base de métal alcalin comprend du sodium ou du potassium déposé sur de l'oxyde de calcium ou de l'oxyde d'aluminium, le catalyseur d'isomérisation comprend une alumine poreuse activée par du carbonate de potassium et le catalyseur de dismutation comprend de l'oxyde de rhénium déposé sur de l'alumine. 15 20
5. Un procédé selon la revendication 4, dans lequel le catalyseur de dismutation est activé avec un tétraalkylétain. 25
6. Un procédé selon la revendication 5, dans lequel le tétraalkylétain est choisi parmi le tétraméthylétain, le tétraéthylétain, le tétrapropylétain, le tétrabutylétain et leurs mélanges. 30

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