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CONVERSION OF OLEFINS

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ABSTRACT OF THE DISCLOSURE

Olefin hydrocarbons are disproportionated by contact with a catalyst comprising a magnesia-titania base promoted with molybdenum oxide, tungsten oxide, molybdenum sulfide, tungsten sulfide, molybdenum hexacarbonyl, tungsten hexacarbonyl and combinations thereof.

This invention relates to the conversion of olefin hydrocarbons. In one aspect it relates to a process for disproportionating an acyclic monoolefinic hydrocarbon free of aryl derivatives containing from 3 to 16 carbon atoms per molecule and mixtures thereof. In another aspect the invention relates to a process for disproportionating an olefin by contact with a catalyst comprising a magnesia-titania base and a promoter selected from the group consisting of molybdenum oxide, tungsten oxide, molybdenum sulfide, tungsten sulfide, molybdenum hexacarbonyl, tungsten hexacarbonyl, and combinations thereof.

By disproportionation according to this invention is meant the conversion of a hydrocarbon into similar hydrocarbons of both higher and lower number of carbon atoms per molecule. When propylene is disproportionated, approximately equimolar quantities of ethylene and butenes are produced. Such an operation is useful in many instances. For instance, a more plentiful hydrocarbon can be converted to a less plentiful and thus more valuable hydrocarbon.

An object of this invention is to convert an olefin feed to hydrocarbons of higher and lower molecular weight. Another object of the invention is to convert an aliphatic monoolefin to similar olefins of higher and lower numbers of carbon atoms. Another object of this invention is to produce ethylene and butenes from propylene. Other aspects, objects and the advantages of my invention are apparent in the written description and the claims.

According to my invention, an olefin hydrocarbon is disproportionated by contact with a catalyst comprising a magnesia-titania base promoted with a compound selected from the group consisting of molybdenum oxide, tungsten oxide, molybdenum sulfide, tungsten sulfide, molybdenum hexacarbonyl, tungsten hexacarbonyl, and combinations thereof. Olefins disproportionated according to the process of this invention include acyclic olefinic hydrocarbons and mixtures thereof. The process is advantageously applied to mono-1- and 2-olefins. The conversion of propylene to ethylene and butene is a feature of the invention.

The magnesia-titania base contains 1–80 weight percent, preferably 20–70 weight percent magnesia and 20–99 weight percent, preferably 30–80 weight percent, titania and preferably has proportions of magnesia and titania corresponding to known chemical compounds including, for example, $MgTiO_3$, $MgTi_2O_5$, $MgTi_3O_7$, Mg_2TiO_4 , Mg_4TiO_6 , and the like. Suitable promoters include molybdenum oxide, tungsten oxide, molybdenum sulfide, tungsten sulfide, molybdenum hexacarbonyl, tungsten hexacarbonyl, and combinations thereof. Although not a promoter in the strict sense, a minor amount of cobalt oxide frequently is beneficial when used with one or more of the above-mentioned oxide promoters.

The catalysts can be prepared by incorporating into a

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magnesia-titania base suitable tungsten or molybdenum compounds by suitable methods such as, for example, impregnation, dry mixing, or coprecipitation. Suitable tungsten and molybdenum compounds include tungsten oxide, molybdenum oxide, tungsten sulfide, molybdenum sulfide, molybdenum hexacarbonyl and tungsten hexacarbonyl and compounds convertible to these materials in the activation steps. Sufficient promoter is used to obtain the desired activity. Since the molybdenum and tungsten compounds usually are more expensive than the base material, unnecessarily large amounts are ordinarily not used. Generally, the finished catalyst contains from 0.1–30 weight percent of the promoter, preferably 1–15 weight percent. The finished catalyst can be in the form of powders, granules, agglomerates, pellets, spheres, extrudates, and the like, depending upon the type of contacting technique employed in the reaction. The catalysts of this invention can contain other materials which do not substantially promote unwanted reactions or reduce the activity for disproportionation. For example, the catalyst can contain substantial amounts of inert materials in amounts which do not change the central characteristics of the disproportionation reaction.

The promoted catalyst compounds can be activated by any suitable technique which permits activation for disproportionation. For example, molybdenum oxide (or compounds convertible to these on calcination) can be impregnated on a magnesia-titania gel followed by calcination in air at temperatures of 700–1600° F. for 0.5–20 hours. Tungsten oxide can be ball-milled together with the magnesia-titania followed by heating in an inert gas such as nitrogen for 0.5–20 hours at 800–1400° F. Molybdenum hexacarbonyl can be impregnated, using a non-aqueous solvent such as benzene, on a magnesia-titania base which has previously been activated by calcination in air. The carbonyl impregnated solid is further prepared for disproportionation activity by drying up to 500° F. in an inert atmosphere. It will be understood that, when the magnesia-titania is associated with one or more of the above-named promoters and is given a suitable activation treatment, the finished catalyst may contain a species whose identity is not completely recognized. Therefore, the catalytic agent is the reaction product resulting from admixture of the material and the activation treatment. The catalyst can be regenerated by contact with diluted air to remove accumulated coke under controlled conditions and by a treatment similar to the initial activation treatment if necessary.

The disproportionation process can be carried out either batch-wise or continuously using a fixed catalyst bed, stirred batch reactor, a fluidized catalyst chamber, or other suitable contacting techniques. The process can be carried out in the vapor or liquid phase at temperatures from 150–600° F. Generally the disproportionation reaction of this invention is essentially independent of pressure, except as pressure affects the density of the feed and thus the contact time, but is operated effectively at pressures of 0–1500 p.s.i.g. Weight hourly space velocities of 0.1–300 wt. feed/wt. catalyst/hour are suitable. The operable range of contact time for the process of this invention depends primarily upon the operating temperature and the activity of the catalyst, which is influenced by surface area, promoter concentration, activation, temperature, etc. Conditions and contact times are selected to obtain high efficiencies of conversion to the desired products. In general, lower space rates and longer contact times are associated with lower temperatures. In batch reactions, the catalyst comprises from about 1 to about 40 weight percent of the reaction mixture and reaction times of about 1 minute to 20 hours are used. If desired, paraffinic and cycloparaffinic hydrocarbons having up to

12 carbon atoms per molecule can be employed as diluents for the reaction.

Suitable feeds for the process of this invention include acyclic olefinic hydrocarbons containing from 3 to 16 carbon atoms per molecule and mixtures thereof. The process is most advantageously applied to mono-1- and 2-olefins. The conversion of propylene is an especially valuable process according to my invention. The feed should be essentially free of impurities which adversely affect the reaction.

Following the reaction period, any suitable method can be used to separate the hydrocarbon phase from the solid catalyst phase and to recover the products. For example, techniques such as fractional distillation, solvent extraction, absorption, and the like, can be employed for the separation of products. Unconverted feed materials, diluents, or products not in the desired molecular weight range can be recycled.

The following example is illustrative of the practices of this invention, but is not intended to unduly limit the invention. Throughout these examples, unless otherwise stated, the analyses are in weight percent.

EXAMPLE

The catalyst was prepared as follows: 29.3 parts by weight of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 637 parts by weight of methanol together with 48.0 parts by weight of tetraisopropyl titanate. To this solution was then added 28 parts by weight ammonium hydroxide (28 weight percent aqueous solution) and 18 parts by weight water. A thick white precipitate was observed in about one minute and the resulting gel was allowed to set overnight undisturbed. The gel was then filtered, washed with methanol, dried on a steam bath and further dried for four hours at 1000° F. in a dry nitrogen atmosphere. 4.94 parts by weight of the above-prepared magnesia-titania was then impregnated with a 25 parts by weight aqueous solution containing 0.69 part by weight of ammonium molybdate.

The catalyst was activated by charging 5 parts by volume of the above prepared material into a glass reactor tube and heating at 1000° F. for four hours in the presence of dry flowing air. The air was then replaced with nitrogen and the bed cooled to 200° F. 2 volumes of glass beads preceded the catalyst bed within the reactor.

The catalyst (containing about 10 weight percent molybdenum oxide) was tested for disproportionation activity by passing a stream of propylene over it at atmospheric pressure and at the weight hourly space rate of about 3 lbs. feed/lb. catalyst/hour. The test was carried out at three temperatures. The effluent gases were chromatographically analyzed and gave the following results:

Temperature, ° F.	300	350	400
Ethylene.....	0.3	0.9	0.3
Propylene.....	99.4	97.3	98.5
1-butene.....	0.4	0.5	0.3
trans-2-butene.....	0.2	0.9	0.6
cis-2-butene.....	0.1	0.4	0.3

The presence of ethylene as well as butenes in the reactor effluent indicates that propylene is substantially disproportionated using this catalyst and conditions.

Reasonable variation and modification are possible within the scope of this invention which sets forth a process and catalyst for disproportionating olefins.

I claim:

1. A process which comprises disproportionating at least one acyclic monoolefin hydrocarbon free of aryl substituents having from 3 to 16 carbon atoms per molecule, by contacting said olefin with a catalyst consisting essentially of a magnesia-titania base promoted with a compound selected from the group consisting of molybdenum oxide, tungsten oxide, molybdenum sulfide, tungsten sulfide, molybdenum hexacarbonyl, tungsten hexacarbonyl, and combinations thereof, under conditions, including conditions of temperature, pressure and contact time, suitable for obtaining a disproportionated product.

2. A process for disproportionating an acyclic monoolefin hydrocarbon free of aryl substituents having from 3 to 16 carbon atoms per molecule, by contacting said olefin with a catalyst consisting essentially of a magnesia-titania base and a promoter selected from the group consisting of molybdenum oxide, tungsten oxide, molybdenum sulfide, tungsten sulfide, molybdenum hexacarbonyl, tungsten hexacarbonyl and combinations thereof to produce a disproportionated product, under conditions, including conditions of temperature, pressure and contact time, suitable for obtaining a disproportionated product, within a temperature range of 150–600° F. and a pressure range of 0–1500 p.s.i.g.

3. The process of claim 2 wherein said catalyst consists essentially of a base comprising 1–80 weight percent magnesia, 20–99 weight percent titania, and the promoter comprises 0.1–30 weight percent of the base.

4. The process of claim 2 wherein said catalyst consists essentially of a base comprising 20–70 weight percent magnesia, and 30–80 weight percent titania, and the promoter comprises 1–15 weight percent of the catalyst.

5. The process of claim 2 wherein said olefin is propylene and said disproportionated product comprises ethylene and butene.

6. The process of claim 3 wherein said olefin is propylene and said disproportionated product comprises ethylene and butene.

7. The process of claim 4 wherein said olefin is propylene and said disproportionated product comprises ethylene and butene.

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