products can be used as feedstocks for other valuable petrochemicals. The Bayer process operates at 100°C with an ionic exchange resin catalyst to give 75% of dimers and 25% of trimers with high conversion ratio from isobutene. The dimerization and oligomerization of linear butene with UOP's Octol process using phosphoric acid physically absorpted on a support or IFP's Dimersol X process based on a nickel salt/aluminum alkyls catalyst gave less branched octenes which are useful for the preparations of plasticizers. Selective dimerization of isobutene are particular interested by industry since the separation of individual butene isomers appear difficult especially for isobutene and 1-butene which almost have identical boiling points. One method to separate isobutene from mixed butenes involves the selective dimerization or oligomerization of isobutene. HPA dissolved in water has been reported as effective catalysts for such process. Traces amount of isobutene in C4 mixtures can be removed by such HPA or its salts such as Cr^{3+}, La^{3+}, Al^{3+}, Fe^{3+}, Cu^{2+}, Cd^{2+}, Ca^{2+}, and Zn^{2+} through selective isobutene dimerizations as well. However, due to the corrosive nature of HPA, the processes using the unsupported HPA often require high maintenances. Solid acid or supported catalysts are preferred for industrial processes since such process is less hazardous and more easily to be operated. Unfortunately, when HPA or its water soluble salts is supported directly, on SiO_2 for example, the acid strength decreases. Therefore, a lower activity using supported HPA catalysts for olefin dimerization is expected. Such supported HPA acids have been reported in the literature and used to catalyze the light olefin dimerizations and oligomerizations since the eighties. JP 57014538A teaches selective oligomerizations of isobutene into polyisobutene from a mixtures of 1-butene and isobutene using HPA or its salt as catalyst at 70°C. Only isobutene was oligomerized with 99.3% conversion and 99.9% selectivity for the oligomer.

As described herein before, there is a need to develop other means to replace MTBE and ethanol in gasoline as an octane enhancer. Also there is a need to replace MTBE, ethanol or alkylates as RON stabilizers or enhancers.

However, there are issues involving maintenance, leaching out of catalysts, lower inefficient activities of catalysts, and poor selectivity which need to be addressed.

Further, solution HPA can be used to catalyze the light olefin oligomerizations effectively. However, such catalysts are corrosive in nature and require high maintenances. In addition, supported HPA have been used in selective isobutene dimerization/oligomerization to produce isobutene dimers/ trimers. Such catalysts are prone to be leached out, deactivation and having lower activities comparing to free HPA.

The present invention provides metal salts of heteropolyacid unsupported solid catalyst compositions useful for the production of butene dimers and/or oligomers through dimerization and oligomerization of mixed butenes.

Summary

The present invention is directed in one aspect to a process of using an unsupported metal (e.g., cesium) substituted heteropolyacid catalyst composition for the production of butene dimers and/or oligomers from mixed butenes, in which, under mild conditions and in the presence of the catalyst, all isomers of the mixed butenes produce highly branched C8 and C8+ olefins. The mixture of C8 olefins in this invention is mixed octenes, which are dimers of mixed butenes. C8+ olefins

utilized as premium feeds for Fluid Catalytic Cracking (FCC) processes such as Deep Catalytic Cracking (DCC) and High Severity Fluid Catalytic Cracking (HSFCC) processes to produce highly demanded light olefins such as ethylene and propylene. A mixture of dimers and trimers which have a large number of allylic hydrogens are considerably more reactive and have proven to be the most desirable feeds for FCC based cracking processes such as HSFCC and DCC. These C8 and C8+ products may also be used as intermediates in synthesizing detergent, plasticizer, pesticide, lubricants, additives, flavors, medicine and many other fine industrial chemicals.

Examples

The invention will be more fully described in conjunction with the following specific examples which are not to be construed as limiting the scope of the invention.

The following experiments were conducted at a pilot plant having the configuration and characteristics of the system 100 illustrated in Fig. 1.

The mixed butenes feed stream was used without any purification and the composition of the mixed butenes feed can be: 1-butene (about 21%); isobutene (about 35%); 2-cis-butene (about 19%); and 2-trans-butene (about 25%). All percentages mentioned herein are based on weight unless otherwise noted.

Example 1

Synthesis of the $Cs_{2.2}H_{0.8}PMo_{12}O_{40}$ Catalyst

CLAIMS

1. A process for dimerizing and oligomerizing a hydrocarbon feed comprising mixed olefins to produce mixed branched higher olefins, said process comprising the steps of:

introducing the hydrocarbon feed into a reactor vessel under oligomerization conditions;

contacting the mixed hydrocarbon feed with a catalyst within the reactor vessel to convert the mixed olefins into the mixed branched higher olefins, wherein the catalyst comprises an unsupported metal substituted heteropolyacid catalyst represented by the following formula:

$$Cs_xH_yPMo_{12}O_{40}$$

wherein, x and y represent numbers; and

producing a product stream comprising the mixed higher olefins from the reactor vessel;

wherein the hydrocarbon feed comprises at least two butenes and the mixed higher olefins comprises olefins having more than 4 carbons.

2. The process of claim 1, wherein the mixed olefins consist essentially of butene isomers.

3. The process of claim 1, wherein the oligomerization conditions are about 40°C and isobutene is selectively oligomerized from the mixed olefins to at least substantially form diisobutene as the product stream.

4. The process of claim 1, wherein the oligomerization conditions are greater than 80°C and all isomers of mixed butenes which comprise the mixed olefins are oligomerized from the mixed olefins to form the product stream comprising olefins having 8 carbons and olefins having more than 8 carbons.

5. The process of claim 1, wherein x is $0< x <5$ and y is $0< y <5$.

6. The process of claim 1, wherein $3>x>2$ and $0<y<1$.

7. The process of claim 1, wherein the mixed higher olefins of the product stream comprise at least about 50% by weight olefins having 8 carbons.

8. The process of claim 1, where the reactor vessel is maintained at a temperature of between about 40-300°C.

9. A process for producing a fuel composition from mixed butenes using a butene dimerization/oligomerization system, the process comprises the step of:

introducing a feed stream comprising the mixed butenes into a reactor vessel under oligomerization conditions;

contacting the mixed butenes feed stream with a catalyst within the reactor vessel to convert the mixed butenes into mixed higher olefins that comprise olefins having at least 8 carbons, wherein the catalyst comprises an unsupported metal substituted heteropolyacid catalyst represented by the following formula:

$$Cs_xH_yPMo_{12}O_{40}$$

wherein, x and y represent numbers;

producing a product stream comprising the mixed higher olefins from the reactor vessel; and

combining the product stream with a fuel component to produce the fuel composition;

wherein the fuel component comprises gasoline, diesel, jet fuel, aviation gasoline, heating oil, bunker oil, or a combination thereof.

10. The process of claim 1, wherein the process is a single stage process occurring in the reactor vessel and wherein the mixed butenes are converted into the mixed higher olefins as a result of a single pass through the reactor vessel.

11. The process of claim 9, wherein the feed stream is a discharge stream from a FCC unit, a thermal cracking unit, a raffinates stream from an MTBE process, a raffinates stream from a TBA process, a liquefied petroleum gas (LPG) stream, or a combination thereof.

12. The process of claim 9, wherein the mixed butenes comprises at least two butene isomers.

13. The process of claim 9, wherein $3>x>2$ and $0<y<1$.