U.S. Patent 5,874,380, assigned to Exxon Chemical Patents, Inc., claims a solid state insoluble salt catalyst system for the carbocationic polymerization of olefin monomer in the presence of polar or non-polar reaction medium which comprises at least one salt of a strong acid and a carbocationically active transition metal catalyst selected from Groups IIIA, IVA, VA, and VIA of the Periodic Table of the Elements.

U.S. Patent No. 6,384,154, assigned to BASF Aktiengesellshaft, discloses a process for preparing halogen free, reactive polyisobutylene by cationic polymerization over an acidic, halogen free heterogeneous catalyst comprising oxides and elements from transition or main group I, II, III, IV, V, VI, VII or VIII of the Periodic Table of the Elements. The polymerization is carried out in a fixed bed reactor.

The solid, heterogeneous butylene polymerization catalysts cited above do solve the problem of catalyst residues in the reactor effluent, thereby eliminating the need for post reaction treatment. However, conversions are low, space velocities are low and reaction temperatures are low.

BF_3 activated metal oxides are not described in the prior art as polymerization catalysts for the manufacture of polybutene or polyisobutylene. In fact, U.S. Patent 6,710,140 assigned to BASF Aktiengesellshaft, claims the use of alumina as a solid deactivator to absorb BF_3 catalyst residues from polyisobutylene reactor effluents. The resulting BF_3-alumina complex is described to be not catalytic.

Summary ~~of the Invention~~

In accordance with the concepts and principles of the present disclosure~~invention of the present application~~, a process is provided for preparing an improved catalyst system which may be used in connection with acid catalyzed organic compound conversion reactions. This catalyst system desirably comprises a BF_3/alcohol-metal oxide reaction product having increased activity over catalyst compositions obtained using other processes and methods. The BF_3/alcohol-metal oxide reaction products of the present disclosure~~invention~~ are stable at operating conditions and the organic conversion products made using these catalyst systems do not contain catalyst residues and are free from boron and fluorine residues. Because the conversion products do not contain catalyst residues, post reaction catalyst removal is not required. Thus, heterogeneous production processes are greatly simplified through the use of the catalyst systems of the invention of the present application.

In one aspect of the present disclosure, there is provided a catalyst system for heterogeneous catalysis of an isobutylene polymerization reaction to form a polyisobutylene product, the catalyst system comprising a reaction product of (i) a BF_3/alcohol catalyst complex and (ii) an alumina support for said catalyst complex, a concentration of said catalyst complex on said alumina support ranges between 10 to 30% by weight, a ratio of the alcohol to the BF_3 in said catalyst complex ranges between 0.5 mole of the alcohol per mole of BF_3 to 2 moles of the alcohol per mole of BF_3.

The catalyst systems of the present disclosure~~invention~~ are particularly applicable to the heterogeneous catalytic polymerization of isobutylene in isobutylene containing streams to

thereby produce polyisobutylenes, and even more particularly, highly reactive polyisobutylenes (HR PIB).

The catalyst systems of the present disclosure~~invention~~ are particularly well suited for use in connection with the conduct of acid catalyzed reactions such as dimerization and oligomerization of olefins.

In accordance with the concepts and principles of the present disclosure~~invention~~, a highly stable catalyst system is provided for heterogeneous catalysis of organic compound conversion reactions. The system may desirably include a reaction product of (i) a BF_3/alcohol catalyst complex and (ii) an activated metal oxide support for the catalyst complex. The reaction product, which may be referred to as a BF_3/alcohol-metal oxide system, includes an amount of the catalyst complex effective for catalyzing conversion reactions. In particular, the catalyst system of the present disclosure~~invention~~ is useful in connection with conversion reactions such as Friedel-Crafts alkylation, phenolic alkylation, olefin dimerization, olefin oligomerization, olefin polymerization, propylene oligomerization, propylene polymerization, butylene dimerization, butylene oligomerization, isobutylene dimerization, isobutylene oligomerization, butylene polymerization, isobutylene polymerization or isoparaffin alkylation. The catalyst systems of the present disclosure~~invention~~ are highly stable and are generally not consumed during the reaction. That is to say, the catalyst systems of the present disclosure~~invention~~ do not require regeneration. Moreover, when the catalyst systems of the present disclosure~~invention~~ are used in the form of a fixed bed, there is generally no need for treatment of the product for removal of catalyst residues.

Preferably, the alcohol of the catalyst system has no alpha hydrogen. Even more preferably the alcohol may comprise a C_1-C_{10} monohydric alcohol, glycol or polyhydric alcohol. Ideally the alcohol may be methanol.

Preferably the concentration of the catalyst complex on the alumina may range from about 10 to about 30 % by weight. Ideally the concentration of the catalyst complex on the alumina may range from about 25 to about 30 % by weight.

In a preferred embodiment of the present disclosure~~invention~~, the catalyst system may be used in the form of a fixed bed, the activated metal oxide support may comprise gamma alumina, and the conversion reaction may comprise polymerization of isobutylene to form a polyisobutylene product.

Desirably the ratio of alcohol to BF_3 in the catalyst complex may range from about 0.5 mole of alcohol per mole of BF_3 to about 2 moles of alcohol per mole of BF_3.

Ideally the ratio of alcohol to BF_3 in the catalyst complex may range from about 1 mole of alcohol per mole of BF_3 to about 1.3 moles of alcohol per mole of BF_3.

In a highly preferred embodiment of the present disclosure~~invention~~, a catalyst system is provided for the heterogeneous catalysis of an isobutylene polymerization reaction and the system comprises a reaction product of (i) a BF_3/methanol catalyst complex and (ii) a gamma alumina support for said catalyst complex. In this highly preferred form of the present disclosure~~invention~~, the ratio of alcohol to BF_3 in the catalyst complex may range from about 0.5 mole of alcohol per mole of BF_3 to about 2 moles of alcohol per mole of BF_3, and the concentration of the catalyst complex on the alumina may range from about 10 to about 30 % by weight. Moreover, the catalyst system is ideally used in the form of a fixed bed.

The present disclosure provides~~In accordance with the another aspect of the invention,~~ a method ~~is provided~~ for preparing a catalyst system for heterogeneous catalysis of an organic compound conversion reaction. This method comprises reacting (i) a BF_3/alcohol catalyst complex and (ii) an activated metal oxide support for said catalyst complex. The reaction product includes an amount of the catalyst complex effective for catalyzing conversion reactions.

Desirably the alcohol has no alpha hydrogen. Even more desirably, the alcohol may be methanol.

Preferably the concentration of the catalyst complex on the alumina may range from about 10 to about 30 % by weight.

In a preferred form of the present disclosure~~invention~~, the conversion reaction may comprise the polymerization of isobutylene to form a polyisobutylene product, the activated metal oxide support may comprise gamma alumina, and the ratio of alcohol to BF_3 in the catalyst complex may range from about 0.5 mole of alcohol per mole of BF_3 to about 2 moles of alcohol per mole of BF_3.

In a highly preferred form of the present disclosure~~invention~~, a method is provided for preparing a catalyst system for heterogeneous catalysis of an isobutylene polymerization reaction. In accordance with this highly preferred form of the present disclosure~~invention~~, the method comprises reacting (i) a BF_3/methanol catalyst complex and (ii) a gamma alumina support for said catalyst complex. Ideally the ratio of alcohol to BF_3 in the catalyst complex may range from about 0.5 mole of alcohol per mole of BF_3 to about 2 moles of alcohol per mole of BF_3, and the concentration of the catalyst complex on the alumina may range from about 10 to about 30 % by weight.

The present disclosure~~invention~~ also provides a method for conducting an organic compound conversion reaction wherein a selected reactive organic compound is contacted with a catalyst system as set above. In particular, the present disclosure~~invention~~ provides a method for conducting an isobutylene polymerization reaction which comprises contacting isobutylene with a catalyst system that comprises a reaction product of (i) a BF_3/methanol catalyst complex and (ii) a gamma alumina support for said catalyst complex In this highly preferred form of the present disclosure~~invention~~, the ratio of alcohol to BF_3 in the catalyst complex may range from about 0.5 mole of alcohol per mole of BF_3 to about 2 moles of alcohol per mole of BF_3, and the concentration of the catalyst complex on the alumina may range from about 10 to about 30 % by weight. Moreover, the catalyst system is ideally used in the form of a fixed bed.

Detailed Description of the Invention

The object of the invention is to provide an activated metal oxide catalyst composition or system that may be used in a wide range of organic compound conversion reactions requiring an acid catalyst. Organic conversion reactions may include, but are not limited to, Friedel-Crafts alkylation, phenolic alkylation, olefin dimerization and oligomerization, olefin polymerization, propylene oligomerization and polymerization, butylenes and isobutylene dimerization and oligomerization, butylenes and isobutylene polymerization, isoparaffin alkylation and the like.

A preferred embodiment of this invention is to provide a heterogeneous catalyst composition or system for the dimerization and oligomerization of higher alpha-olefins in the range of C_5-C_{12}. Such products may be useful as synthetic lubricant intermediates, particularly for the manufacture of polyalphaolefins (PAO) based on dimerization and oligomerization of C_{10}-C_{12} alpha-olefins.

A particularly preferred embodiment of the invention is to provide an efficient, heterogeneous catalyst system for the polymerization of isobutylene to produce highly reactive polyisobutylene.

Activated metal oxide catalysts of the invention of the present application are prepared by reacting normally liquid BF_3/alcohol complexes with anhydrous crystalline aluminum oxide (alumina). Gamma and theta alumina are the preferred crystalline structures.

BF_3-alumina compositions of the prior art either are not catalytic for some organic conversion reactions, as reported in U.S. Patent 6,710,140. Moreover, in some cases at BF_3 levels that might be catalytic, the BF_3 leaches off and requires additional BF_3 to be added along with the reactant feed. This, of course, defeats the purpose of a solid