CATALYTIC CONVERSION OF METHANE AND NATURAL GAS TO CONDENSABLE HYDROCARBONS

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ABSTRACT

Catalytic processes are taught for oxidative chemical conversion of gaseous reactants comprising methane, natural gas or other gaseous compounds combined with air or oxygen to products and catalytic methanation of resulting oxidized products comprising alcohols, aldehydes, ketones, glycol ethers and aldehyds to condensable hydrocarbons using methane, natural gas or other gaseous hydrocarbons. Gaseous reactants including methane, ethene, propane, oxides of carbon, unsaturated compounds and other organic compounds with conversion to condensable hydrocarbons by this catalytic process. The catalysts are based on di-metal, tri-metal and/or poly-metal backbone or molecular string type compounds of transition metals, comprising titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, molybdenum, ruthenium, rhodium, palladium, silver, hafnium, tantalum, tungsten, rhenium, osmium, iridium, platinum, gold and combinations thereof in conjunction with a non-fluoride magnesium halide.
CATALYTIC CONVERSION OF METHANE AND NATURAL GAS TO CONDENSABLE HYDROCARBONS

BACKGROUND

[0001] 1. Field of Invention

[0002] This invention relates to catalytic conversion of carbon-containing gaseous compounds including methane, natural gas and other gaseous carbon-containing compounds to condensable alkanes and alkenes with catalysts based on molecular strings of di-, tri- and/or poly-groups of bonded transition metal complexes in conjunction with a non-fluoride salt comprising magnesium halides.

[0003] 2. Description of Prior Art

[0004] A number of catalytic chemical processes have been reported for partial oxidation of methane. Methanol is often a product of partial oxidation while formaldehyde may also be produced. These processes specifically exclude conversion of synthesis gas to products since they are not products of methane conversion, rather employ hydrogen as a reductive co-reactant. Controlled air oxidation of certain gaseous hydrocarbons may produce small amounts of aldehydes, however such processes have not been identified as economically viable. Formaldehyde formation by direct air oxidation of methane has not previously been productive.

[0005] There are a limited number of catalytic reactions described in the scientific and patent literature for conversion of methane to a range of low concentration products from carbon oxides to polymeric residues that include small amounts of formaldehyde. Methanol has been formed by dissolving methane in a solvent using a RuO catalyst at 2°C to 60°C, 5 to 20 atmospheres pressure, in 30 minutes to 30 hours in the presence of controlled amounts of air as taught by U.S. Pat. No. 5,347,057, issued Sep. 13, 1994, U.S. Pat. No. 5,336,826, issued Aug. 9, 1994, each teaches a process for the selective oxidation of methane to higher molecular weight hydrocarbons in the vapor phase in a quartz reactor at 600°C to 800°C over Li doped catalyst of niobia, zirconia, thoria, tantalum or boria. Less selective chemistry may oxidize methane to carbon oxides and low concentrations of byproducts.

[0006] Catalytic reduction of aldehydes, alcohols and other compounds to hydrocarbons has been conducted previously with the nearly exclusive use of hydrogen gas. Hydrogen gas is commonly manufactured from hydrocarbons such as methane with the loss of carbon or from carbon and water at high temperature by a steam reformation process. Production of hydrogen by these processes is expensive but may be less expensive than the electrolytic process. Natural gas and methane are available renewable resources, although natural gas is presently taken from underground wells.

[0007] A number of other chemical reaction paths have previously been investigated for use of methane as a reactant including controlled oxidation of methane to alcohols and aldehydes, chlorination of methane to make reactive intermediates and application of methane sulfonic acid to produce methylated compounds. Chlorination of methane has also been conducted, however formation of higher molecular weight hydrocarbons may be conducted with formation of metal chlorides, hydrogen chloride or other chlorinated compounds resulting in a loss of chlorine, its acids or its salts. In the chemical industry, methane has been a raw material for the manufacture of methanol (CH₃OH), formaldehyde (CH₂O), nitromethane (CH₃NO₂), chloroform (CHCl₃), carbon tetrachloride (CCl₄), and some freons. The reactions of methane with chlorine and fluorine are triggered by light. When exposed to bright visible light, mixtures of methane with chlorine or fluorine react explosively. Application of methane sulfonic acid as a viable reactant is of limited use and produces sulfuric acid as a by product. The aforementioned methane reaction routes are expensive, produce significant byproducts and hazardous waste residues.

[0008] Reaction of methane with other organic compounds has long been sought as a method of obviating the need for hydrogen gas but such reactions have not been accomplished in economically viable processes. Current industrial chemical methane processes generate synthesis gas, halocarbons, hydrogen cyanide, acetylene, carbon disulfide and carbon but reaction efficiencies for production of saturated hydrocarbons are quite low and may be conducted only in the presence of hydrogen gas.

[0009] The present application teaches use of methane and natural gas as direct reducing agents for carbon oxides, formaldehyde and other oxidized low carbon number gaseous compounds resulting in formation of condensable hydrocarbons using selected catalysts. For example, catalytic methane reduction or methanation of formaldehyde to condensable hydrocarbons proceeds readily at elevated temperatures and modest pressure. Typical products include ethylene, propane and similar products.

[0010] It is an object of this invention, therefore, to provide a molecular string type transition metal catalytic process for methanation of partially oxidized compounds resulting in formation of condensable gaseous hydrocarbons.

[0011] It is another object of this invention to provide a molecular string type transition metal catalytic process for conversion of methane and natural gas to condensable hydrocarbons.

[0012] It is still another object of this invention to provide molecular string type transition metal catalysts in conjunction with a non-fluorinated magnesium halide for direct production of condensable hydrocarbons including ethylene, propane and other hydrocarbons.

[0013] Other objects of this invention will be apparent from the detailed description thereof which follows, and from the claims.

SUMMARY OF THE INVENTION

[0014] This invention describes catalytic oxidative chemical conversion of gaseous reactants including methane, natural gas or other gaseous hydrocarbons combined with air or oxygen to products and subsequent catalytic methanation of resulting oxidized products comprising alcohols, aldehydes and other carbon compounds to condensable hydrocarbons using methane, natural gas or other gaseous hydrocarbon reducing agents using selected members of a family of transition metal catalysts, based on a di-metal, tri-metal and/or poly-metal backbone or string type compounds in conjunction with a non-fluorinated magnesium halide promoter. These catalysts have been effectively demonstrated to be active for formation of condensable hydrocarbons.

DETAILED DESCRIPTION OF THE INVENTION

[0015] A process is taught for catalytic oxidative chemical conversion of gaseous reactants comprising methane, natural gas or other gaseous hydrocarbons combined with air or oxygen to products and catalytic methanation of resulting oxidized products comprising alcohols, aldehydes, ketones,
glycol ethers and alcohols to condensable hydrocarbons using
methane, natural gas or other gaseous hydrocarbon reducing
agents, catalysts being made from di-metal, tri-metal and/or
poly-metal backbone or molecular string type compounds of
transition metals, comprising titanium, vanadium, chromium,
manganese, iron, cobalt, nickel, copper, zirconium, niobium,
molybdenum, ruthenium, rhodium, palladium, silver,
hafnium, tantalum, tungsten, rhenium, osmium, iridium,
platinum, gold and combinations thereof in conjunction with
a promoter comprising magnesium salt comprising magne-
sium chloride, bromide or iodide. No hydrogen gas, strong
oxidizing acids such as sulfuric or fuming sulfuric acid or
emissive radiation source for any type including electric current,
microwaves, x-rays or ionizing radiation were employed.
Catalysts, such as [vanadium]₃, [manganese]₃, or [cobalt]₃,
type compounds, for which the transition metals and directly
attached atoms possess C₃v, D₆h or D₆d point group symme-
try. These catalysts have been designed based on a formal
theory of catalysis, and the catalysts have been produced, and
tested to prove their activity. The theory of catalysis rests
upon a requirement that a catalyst possess a single metal atom
in the molecular string such that transitions from one molecular
configuration to another does not occur during instructions
may proceed freely to products as driven by thermodynamic
considerations. Catalysts effective for partial oxidation of
methane, natural gas or other gaseous hydrocarbons to alde-
hydes and other products can be made from mono-metal,
di-metal, tri-metal and/or poly-metal backbone or molecular
string type compounds of the transition metals comprising
titanium, vanadium, chromium, manganese, iron, cobalt,
nickel, copper, zirconium, niobium, molybdenum, ruthen-
uim, rhodium, palladium, silver, hafnium, tantalum, tung-
sten, rhenium, osmium, iridium, platinum, gold and/or
combinations thereof. These catalysts are made in the absence
of oxygen so as to produce compounds wherein the oxidation
state of the transition metal is low, typically monovalent or
divalent although trivalent metal catalysts may also be
effective. Anions employed for these catalysts comprise fluoride,
chloride, bromide, iodide, cyanide, sulfate, phosphate,
borate, oxide, hydroxide, oxalate, acetate, organic chelating
agents and/or other groups. Mixed transition metal compo-
ounds have also been found to be effective catalysts for
oxidative or reductive chemical conversions.

[0016] The catalysts act on oxygen in the presence of meth-
ane forming aldehydes, other partially oxidized carbon prod-
ents and water. Methane or natural gas is catalytically oxy-
dized to formaldehyde under conditions of higher
temperature and modest pressure. For example methane is
catalytically oxidized to formaldehyde using a cobalt (II)
oxalate catalyst on a silica alumina support in a temperature
range of 350°C to 400°C, while ethane is catalytically
converted to acetaldehyde and other products under similar
conditions.

[0017] The process for catalytic reduction of polar organic
compounds such as alcohols, aldehydes, alcohols and other
carbon compounds using methane, natural gas or other gas-
eous hydrocarbons is a general process designed to replace
hydrogen in production of condensable hydrocarbons. The
process is based on catalysts possessing multiple metal type
transition metal compounds, such as [iron]₃ or [manganese]₃
type compounds and numerous others in conjunction with
non-fluorinated magnesium halide promoter. Different first
row transition metal catalysts have been prepared for conver-
sion of methane to condensable organic compounds at mod-
est pressures and at temperatures of 350°C to 400°C. Reac-
tion pressures of 0 to 60 psi have been employed in several of
the catalytic methane conversion processes, although higher
pressures are also effective. This process may also be
employed for reduction of carbon oxides forming hydrocar-
bons.

Catalyst Selection Considerations

[0018] The fundamentals of catalysis effort forms a basis
for selecting molecular catalysts for specified chemical reac-
tions through computational methods by means of the follow-
ing six procedural steps. An acceptable methanation mecha-
nism, involving a pair of metal atoms, was established for
methane gas in the presence of oxygen or a polar reactant
(step 1). A specific transition metal, such as cobalt, was
selected as a possible catalytic site as found in an M-M or
Co-Co string (step 2), bonded with oxygen or sets of polar
organic molecules in symmetric configurations, and having a
computed bonding energy to the associated polar reactants of
less than –60 kcal/mol (step 3). The first valence state for
which the energy values were two-fold degenerate was
2+(step 4). Acetate, chloride and other anions may be chosen
provided they are chemically compatible with the metal, M
(Co), in formation of the catalyst (step 5). A test should also
be conducted to establish compliance with the rule of 18 (or
32) to stabilize the catalyst so compatible ligands may be
added to complete the coordination shell (step 6). This same
process may be applied for selection of a catalyst using any of
the first, second or third row transition metals, however, only
ones with acceptable low positive or negative bonding ener-
gies can produce effective catalysts. Approximate, computed,
relative bonding energy values may be computed using a
semi-empirical or other algorithm. This computational
method indicated that several of the first row transition metal
complexes can produce usable catalysts once the outer coor-
dination shell has been completed with ligands. Second row
and third row transition metal complexes were also indicated
to produce active catalysts.

[0019] Transition metal catalysts loaded onto silica, silica-
 alumina, alumina or other support materials have been
employed. Non-fluorinated magnesium halide compounds
combined with and/or loaded onto the catalyst support are
effective promoters of the catalytic process. Addition of 0.01
to 90 percent of a catalyst and a balance of non-fluorinated
magnesium halide salts promotes methanation reduction
reactions.

Description of Catalyst Preparation

[0020] Catalyst preparation has been conducted using
nitrogen saturated solvents and nitrogen blanketing to mini-
imize or eliminate air oxidation of the transition metal com-
pounds during preparation. Transition metal catalysts, effective
for conversion of methane, natural gas and other carbon
based compounds to condensable organic compounds, can be
produced by combining transition metal salts in their lowest
standard oxidation states. Thus, such transition metal cata-
lysts can be made by mixing transition metal (1 or II) chlorides
with sodium acetate or ammonium hydrogen oxalate in a 1 to
2 or 1 to 3 ratio, or by forming transition metal compounds in a reduced state by similar means where di-, tri- and/or poly-metal compounds result.

EXAMPLE 1

[0021] The cobalt acetate catalyst may be prepared in a nitrogen atmosphere by addition of 0.15 gram (2 mmol) of ammonium acetate to 0.25 gram (1 mmol) of light pink colored cobalt (II) acetate tetrahydrate dispersed in 15 grams of nitrogen purged ethanol with mixing and gentle heating. To the resulting deep magenta to purple solution was added to 20 grams of a silica alumina support and the mixture was dried under nitrogen producing the catalyst.

EXAMPLE 2

[0022] Preparation of manganese oxalate catalyst may be conducted in a nitrogen atmosphere by addition of 0.28 gram (2 mmol) of ammonium oxalate to 0.20 gram (1 mmol) of manganese (II) chloride tetrahydrate dissolved in 10 grams of nitrogen purged water with mixing. The resulting solution was added 20 grams of silica alumina support and the mixture was dried under nitrogen producing the catalyst.

Catalytic Conversion of Methane to Condensable Hydrocarbons

[0023] The solid cobalt catalyst of example 1 (20 grams) was mixed with approximately 2 grams of manganese chloride and loaded into a one half inch diameter stainless steel reactor tube fit with reactant inlet, pressure and temperature monitoring, product outlet and a means of controlling methane flow rate. In addition, a means of dehydrogenation of the reaction stream was applied. The reactor was flushed with methane and heated to 350° C. to start the reaction. Air addition rates of 0.15 to 0.25 mole per minute at 15 psi in combination with 0.40 to 0.75 mole of methane at 30 psi produced a gas stream of approximately 15 psi flowing through the reactor. Products formed were immediately measured for formaldehyde and condensable hydrocarbons to confirm formation. This process was repeated several times for temperatures in the range of 330° C. to 450° C. and pressures in the range of 30 to 60 psi.

What is claimed:

1. A rapid (less than 30 minutes) process for catalytic oxidative chemical conversion of gaseous reactants comprising methane, natural gas or other gaseous hydrocarbons combined with air, oxygen or polar reactants to products and catalytic methanation of resulting oxidized products comprising aldehydes, ketones, glycol ethers and carbon oxides to condensable hydrocarbons using reactants comprising methane, natural gas or other gaseous hydrocarbon reducing agents, where no hydrogen gas, strong oxidizing agents or electromagnetic energy of any type were employed, catalysts being made from di-metal, tri-metal and/or poly-metal backbone or molecular string type compounds of transition metals, comprising titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zirconium, niobium, molybdenum, ruthenium, rhodium, palladium, silver, hafnium, tantalum, tungsten, rhenium, osmium, iridium, gold and combinations thereof in conjunction with a non-fluoride promoter comprising magnesium chloride, bromide or iodide.

2. A rapid (less than 30 minutes) process for catalytic oxidative chemical conversion of gaseous reactants comprising methane, natural gas or other gaseous hydrocarbons combined with air, oxygen or polar reactants to products and catalytic methanation of resulting oxidized products comprising aldehydes, ketones, glycol ethers and carbon oxides to condensable hydrocarbons using reactants comprising methane, natural gas or other gaseous hydrocarbon reducing agents, where no hydrogen gas, strong oxidizing agents or electromagnetic energy of any type were employed, catalysts being made from di-metal, tri-metal and/or poly-metal backbone or molecular string type compounds of transition metals, comprising titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zirconium, niobium, molybdenum, ruthenium, rhodium, palladium, silver, hafnium, tantalum, tungsten, rhenium, osmium, iridium, platinum, gold and combinations thereof in conjunction with a non-fluoride promoter comprising magnesium chloride, bromide or iodide.

3. A rapid (less than 30 minutes) process for catalytic oxidative chemical conversion of gaseous reactants comprising methane, natural gas or other gaseous hydrocarbons combined with air, oxygen or polar reactants to products and catalytic methanation of resulting oxidized products comprising alcohols, aldehydes, ketones, glycol ethers and carbon oxides to condensable hydrocarbons using reactants comprising methane, natural gas or other gaseous hydrocarbon reducing agents, where no hydrogen gas, strong oxidizing agents or electromagnetic energy of any type were employed, catalysts being made from di-metal, tri-metal and/or poly-metal backbone or molecular string type compounds of transition metals, comprising titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zirconium, niobium, molybdenum, ruthenium, rhodium, palladium, silver, hafnium, tantalum, tungsten, rhenium, osmium, iridium, platinum, gold and combinations thereof in conjunction with a non-fluoride promoter comprising magnesium chloride, bromide or iodide at temperatures between 330° C. and 450° C.

4. A rapid (less than 30 minutes) process for catalytic oxidative chemical conversion of gaseous reactants comprising methane, natural gas or other gaseous hydrocarbons combined with air, oxygen or polar reactants to products and catalytic methanation of resulting oxidized products comprising alcohols, aldehydes, ketones, glycol ethers and carbon oxides to condensable hydrocarbons using reactants comprising methane, natural gas or other gaseous hydrocarbon reducing agents, where no hydrogen gas, strong oxidizing agents or electromagnetic energy of any type were employed, catalysts being made from di-metal, tri-metal and/or poly-metal backbone or molecular string type compounds of transition metals, comprising titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zirconium, niobium, molybdenum, ruthenium, rhodium, palladium, silver, hafnium, tantalum, tungsten, rhenium, osmium, iridium, platinum, gold and combinations thereof in conjunction with a non-fluoride promoter comprising magnesium chloride, bromide or iodide at temperatures between 330° C. and 450° C., and pressures of less than 20 atmospheres.

5. A rapid (less than 30 minutes) process for catalytic oxidative chemical conversion of gaseous reactants comprising methane, natural gas or other gaseous hydrocarbons combined with air, oxygen or polar reactants to products and catalytic methanation of resulting oxidized products comprising alcohols, aldehydes, ketones, glycol ethers and carbon oxides to condensable hydrocarbons using reactants comprising methane, natural gas or other gaseous hydrocarbon reducing agents, catalysts being made from di-metal, tri-metal and/or poly-metal backbone or molecular string type compounds of transition metals, comprising titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zirconium, niobium, molybdenum, ruthenium, rhodium, palladium, silver, hafnium, tantalum, tungsten, rhenium, osmium, iridium, platinum, gold and combinations thereof in conjunction with a non-fluoride promoter comprising magnesium chloride, bromide or iodide.
mium, manganese, iron, cobalt, nickel, copper, zirconium, niobium, molybdenum, ruthenium, rhodium, palladium, silver, hafnium, tantalum, tungsten, rhenium, osmium, iridium, platinum, gold and combinations thereof in conjunction with a non-fluoride promoter comprising magnesium chloride, bromide or iodide at temperatures between 330°C and 450°C.

6. A rapid (less than 30 minutes) process for catalytic oxidative chemical conversion of gaseous reactants comprising methane, natural gas or other gaseous hydrocarbons combined with air or oxygen to products and catalytic methanation of resulting oxidized products comprising alcohols, aldehydes, ketones, glycol ethers and carbon oxides to condensable hydrocarbons using reactants comprising methane, natural gas or other gaseous hydrocarbon reducing agents catalysts being made from di-metal, tri-metal and/or poly-metal backbone or molecular string type compounds of transition metals, comprising titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zirconium, niobium, molybdenum, ruthenium, rhodium, palladium, silver, hafnium, tantalum, tungsten, rhenium, osmium, iridium, platinum, gold and combinations thereof in conjunction with a non-fluoride promoter comprising magnesium chloride, bromide or iodide at temperatures between 330°C and 450°C, and pressures of less than 20 atmospheres.

7. A process for catalytic oxidative chemical conversion of gaseous reactants comprising methane, natural gas or other gaseous hydrocarbons combined with air or oxygen to products and catalytic methanation of resulting oxidized products comprising alcohols, aldehydes, ketones, glycol ethers and carbon oxides to condensable hydrocarbons using reactants comprising methane, natural gas or other gaseous hydrocarbon reducing agents catalysts being made from di-metal, tri-metal and/or poly-metal backbone or molecular string type compounds of transition metals, comprising titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zirconium, niobium, molybdenum, ruthenium, rhodium, palladium, silver, hafnium, tantalum, tungsten, rhenium, osmium, iridium, platinum, gold and combinations thereof in conjunction with a non-fluoride promoter comprising magnesium chloride, bromide or iodide.

8. A process for catalytic oxidative chemical conversion of gaseous reactants comprising methane, natural gas or other gaseous hydrocarbons combined with air or oxygen to products and catalytic methanation of resulting oxidized products comprising alcohols, aldehydes, ketones, glycol ethers and carbon oxides to condensable hydrocarbons using reactants comprising methane, natural gas or other gaseous hydrocarbon reducing agents catalysts being made from di-metal, tri-metal and/or poly-metal backbone or molecular string type compounds of transition metals, comprising titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zirconium, niobium, molybdenum, ruthenium, rhodium, palladium, silver, hafnium, tantalum, tungsten, rhenium, osmium, iridium, platinum, gold and combinations thereof in conjunction with a non-fluoride promoter comprising magnesium chloride, bromide or iodide at temperatures between 330°C and 450°C.

9. A process for catalytic oxidative chemical conversion of gaseous reactants comprising methane, natural gas or other gaseous hydrocarbons combined with air or oxygen to products and catalytic methanation of resulting oxidized products comprising alcohols, aldehydes, ketones, glycol ethers and carbon oxides to condensable hydrocarbons using reactants comprising methane, natural gas or other gaseous hydrocarbon reducing agents catalysts being made from di-metal, tri-metal and/or poly-metal backbone or molecular string type compounds of transition metals, comprising titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zirconium, niobium, molybdenum, ruthenium, rhodium, palladium, silver, hafnium, tantalum, tungsten, rhenium, osmium, iridium, platinum, gold and combinations thereof in conjunction with a non-fluoride promoter comprising magnesium chloride, bromide or iodide at temperatures between 330°C and 450°C, and pressures of less than 20 atmospheres.

10. A process for catalytic chemical conversion of gaseous reactants comprising methane, natural gas or other gaseous hydrocarbons combined with air or oxygen to products comprising condensable hydrocarbons using catalysts made from di-metal, tri-metal and/or poly-metal backbone or molecular string type compounds of transition metals, comprising titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zirconium, niobium, molybdenum, ruthenium, rhodium, palladium, silver, hafnium, tantalum, tungsten, rhenium, osmium, iridium, platinum, gold and combinations thereof in conjunction with a non-fluoride promoter comprising magnesium chloride, bromide or iodide.

11. A process for catalytic chemical conversion of gaseous reactants comprising methane, natural gas or other gaseous hydrocarbons combined with air or oxygen to products comprising condensable hydrocarbons using catalysts made from di-metal, tri-metal and/or poly-metal backbone or molecular string type compounds of transition metals, comprising titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zirconium, niobium, molybdenum, ruthenium, rhodium, palladium, silver, hafnium, tantalum, tungsten, rhenium, osmium, iridium, platinum, gold and combinations thereof in conjunction with a non-fluoride promoter comprising magnesium chloride, bromide or iodide at temperatures between 330°C and 450°C.

12. A process for catalytic chemical conversion of gaseous reactants comprising methane, natural gas or other gaseous hydrocarbons combined with air or oxygen to products comprising condensable hydrocarbons using catalysts made from di-metal, tri-metal and/or poly-metal backbone or molecular string type compounds of transition metals, comprising titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zirconium, niobium, molybdenum, ruthenium, rhodium, palladium, silver, hafnium, tantalum, tungsten, rhenium, osmium, iridium, platinum, gold and combinations thereof in conjunction with a non-fluoride promoter comprising magnesium chloride, bromide or iodide at temperatures between 330°C and 450°C, and pressures of less than 20 atmospheres.