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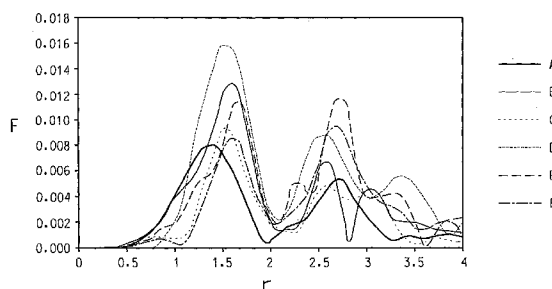
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(54) Title: COPPER-SUBSTITUTED CHROMIUM OXIDE COMPOSITIONS, THEIR PREPARATION, AND THEIR USE AS CATALYSTS AND CATALYST PRECURSORS



(57) Abstract: A crystalline alpha-chromium oxide where from about 0.05 atom % to about 5 atom % of the chromium atoms in the alpha-chromium oxide lattice are replaced by divalent copper (Cu^{+2}) atoms is disclosed. Also disclosed is a chromium-containing catalyst composition comprising as a chromium-containing component the crystalline copper-substituted alpha-chromium oxide; and methods for preparing a composition comprising the crystalline copper-substituted alpha-chromium oxide. One method involves (a) co-precipitating a solid by adding ammonium hydroxide to an aqueous solution of a soluble copper salt and a soluble trivalent chromium salt that contains at least three moles of nitrate per mole of chromium in the solution and has a copper concentration of from about 0.05 atom % to about 5 atom % of the total concentration of copper and chromium in the solution; and after at least three moles of ammonium per mole of chromium in the solution has been added to the solution, (b) collecting the co-precipitated solid formed in (a); (c) drying the collected solid; and (d) calcining the dried solid. Another method involves (a) preparing an aqueous solution of a soluble copper salt and a soluble trivalent chromium salt that contains a copper concentration of from about 0.05 atom % to about 5 atom % of the total concentration of copper and chromium in the solution, (b) evaporating the solution to dryness, and (c) calcining the dried solid. Also disclosed is a chromium-containing catalyst composition comprising a chromium-containing component prepared by treating the crystalline copper-substituted alpha-chromium oxide with a fluorinating agent; and a process for changing the fluorine distribution (i.e., content and/or arrangement) in a hydrocarbon or halogenated hydrocarbon in the presence of a catalyst. The process involves using as the catalyst a composition comprising the crystalline copper-substituted alpha-chromium oxide and/or the treated copper-substituted alpha-chromium oxide.

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TITLE

COPPER-SUBSTITUTED CHROMIUM OXIDE COMPOSITIONS, THEIR PREPARATION, AND THEIR USE AS CATALYSTS AND CATALYST PRECURSORS

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FIELD OF THE INVENTION

This invention relates to chromium-containing compositions and their preparation and use for the catalytic processing of hydrocarbons and/or halogenated hydrocarbons.

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BACKGROUND

It is well known that α -Cr₂O₃ and α -Fe₂O₃ have in common the structure of α -Al₂O₃ (corundum) with the M⁺³ ions occupying octahedral sites in the hexagonally close-packed oxide lattice. In contrast, Cu₂O (Cuprite) has Cu coordinated with 2 oxygen atoms in a cubic structure comprised of two interpenetrating Cu-O networks similar to the Si-O networks in Cristobalite. CuO (tenorite) is a monoclinic crystal structure with Cu atoms located in distorted octahedra with 4 co-planar oxygen atoms at 1.947Å, and 2 apical oxygen atoms at 2.766Å. These basic structures are described in standard treatises; see, for example, pages 538, 543-545, and 550 of *Structural Inorganic Chemistry* by A. F. Wells, 5th ed. Clarendon Press, Oxford, UK (1986). γ -Chromium oxide (CrO_{2.44}) is described in Wilhelmi, *Acta Chemica Scandinavica*, Vol. 22, pages 2565-2573 (1968).

Numerous mixed metal oxides have been prepared in which the cation sites of the lattice are occupied by different metal ions. For example, solid solutions of the type (Cr_xFe_{1-x})₂O₃ are known where 0 < x < 1. These materials have been prepared by standard ceramic or sol-gel techniques as described by Music, et al. in *J. Materials Science*, Vol. 31, pages 4067-4076 (1996) and by Bhattacharya, et al. in *J. Materials Science*, Vol. 32, pages 577-560 (1997).

Various mixed Cr-Cu oxides including copper chromite, copper chromate and copper dichromate are known.

Certain metal oxides are used as catalysts and/or catalyst precursors in the manufacture of fluorinated hydrocarbons. Chromium(III) oxide in particular is useful as it has been found that it may be fluorinated by HF at elevated temperature to give a mixture of chromium fluoride and chromium oxyfluoride species which are active catalysts for conversion of C-Cl bonds to C-F bonds in the presence of HF. This conversion of C-Cl

bonds to C-F bonds by the action of HF, known generally as halogen exchange, is a key step in many fluorocarbon manufacturing processes.

Chromium oxide compositions useful as catalyst precursors may be prepared in various ways or may take various forms. Chromium oxide
5 suitable for vapor phase fluorination reactions may be prepared by reduction of Cr(VI) trioxide, by dehydration of Guignet's green, or by precipitation of Cr(III) salts with bases (see U. S. Patent No. 3,258,500). Another useful form of chromium oxide is hexagonal chromium oxide hydroxide with low alkali metal ion content as disclosed in U. S. Patent
10 No. 3,978,145. Compounds such as MF_4 ($\text{M} = \text{Ti, Th, Ce}$), MF_3 ($\text{M} = \text{Al, Fe, Y}$), and MF_2 ($\text{M} = \text{Ca, Mg, Sr, Ba, Zn}$) have been added to hexagonal chromium oxide hydroxide to increase catalyst life as disclosed in U.S. Patent No. 3,992,325. A form of chromium oxide that is a precursor to a particularly active fluorination catalyst is that prepared by pyrolysis of
15 ammonium dichromate as disclosed in U. S. Patent No. 5,036,036.

The addition of other compounds (e.g., other metal salts) to supported and/or unsupported chromium-based fluorination catalysts has been disclosed. Australian Patent Document No. AU-A-80340/94
discloses bulk or supported catalysts based on chromium oxide (or oxides
20 of chromium) and at least one other catalytically active metal (e.g., Mg, V, Mn, Fe, Co, Ni, or Zn), in which the major part of the oxide(s) is in the crystalline state (and when the catalyst is a bulk catalyst, its specific surface, after activation with HF, is at least $8 \text{ m}^2/\text{g}$). The crystalline phases disclosed include Cr_2O_3 , CrO_2 , NiCrO_3 , NiCrO_4 , NiCr_2O_4 , MgCrO_4 ,
25 ZnCr_2O_4 and mixtures of these oxides. Australian Patent Document AU-A-29972/92 discloses a mass catalyst based on chromium and nickel oxides in which the Ni/Cr atomic ratio is between 0.05 and 5. U.S. Patent Application Publication No. US2001/0011061 A1 discloses chromia-based fluorination catalysts (optionally containing Mg, Zn, Co, and Ni) in which
30 the chromia is at least partially crystalline. Fluorinated catalysts containing cobalt and chromium in combination (e.g. impregnated on a support) are among those disclosed in U.S. Patent No. 5,185,482. U.S. Patent No. 5,559,069 discloses homogeneously dispersed multiphase catalyst compositions characterized by dispersed phases of certain divalent metal
35 fluorides (certain fluorides of Mn, Co, Zn, Mg, and/or Cd) and certain trivalent metal fluorides (fluorides of Al, Ga, V, and /or Cr).

There remains a need for halogen exchange catalysts that can be used for processes such as the selective fluorination and chlorofluorination

of saturated and unsaturated hydrocarbons, hydrochlorocarbons, hydrochlorofluorocarbons, and chlorofluorocarbons, the fluorination of unsaturated fluorocarbons, the isomerization and disproportionation of fluorinated organic compounds, the dehydrofluorination of

5 hydrofluorocarbons, and the chlorodefluorination of fluorocarbons.

SUMMARY OF THE INVENTION

This invention provides a crystalline alpha-chromium oxide where from about 0.05 atom % to about 5 atom % of the chromium atoms in the alpha-chromium oxide lattice are replaced by divalent copper (Cu^{+2})

10 atoms, and a chromium-containing catalyst composition comprising as a chromium-containing component said crystalline copper-substituted alpha-chromium oxide.

This invention also provides a co-precipitation method for preparing a composition comprising said crystalline copper-substituted alpha-chromium oxide. The method comprises (a) co-precipitating a solid by
15 adding ammonium hydroxide (aqueous ammonia) to an aqueous solution of a soluble copper salt and a soluble trivalent chromium salt that contains at least three moles of nitrate (i.e., NO_3^-) per mole of chromium (i.e., Cr^{3+}) in the solution and has a copper concentration of from about 0.05 atom %
20 to about 5 atom % of the total concentration of copper and chromium in the solution; and after at least three moles of ammonium (i.e., NH_4^+) per mole of chromium (i.e., Cr^{3+}) in the solution has been added to the solution, (b) collecting the co-precipitated solid formed in (a); (c) drying the collected solid; and (d) calcining the dried solid.

25 This invention also provides a thermal method for preparing a composition comprising said crystalline copper-substituted alpha-chromium oxide. The method comprises (a) preparing an aqueous solution of a soluble copper salt and a soluble trivalent chromium salt that contains a copper concentration of from about 0.05 atom % to about 5
30 atom % of the total concentration of copper and chromium in the solution; (b) evaporating the solution to dryness; and (c) calcining the dried solid.

This invention also provides a chromium-containing catalyst composition comprising a chromium-containing component prepared by treating said crystalline copper-substituted alpha-chromium oxide with a
35 fluorinating agent (e.g., hydrogen fluoride).

This invention also provides a process for changing the fluorine distribution (i.e., content and/or arrangement) in a hydrocarbon or halogenated hydrocarbon in the presence of a catalyst. The process is

characterized by using as the catalyst a composition comprising at least one chromium-containing component selected from the group consisting of said crystalline copper-substituted alpha-chromium oxides and said treated copper-substituted alpha-chromium oxides.

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BRIEF DESCRIPTION OF THE DRAWING

Figure 1 represents a plot of the radial distribution function (i.e., the probability of finding an atom at a certain distance, r , from a central atom) associated with the local atomic structure around (a) a copper central atom in Cu_2O , (b) a copper central atom in CuO , (c) a copper central atom in $\text{Cu}_2\text{Cr}_2\text{O}_5$, (d) a chromium central atom in Cr_2O_3 , (e) copper in a sample of copper-substituted alpha-chromium oxide nominally containing 1 atom % copper and (f) copper in a sample of copper-substituted alpha-chromium oxide nominally containing 2 atom % copper.

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DETAILED DESCRIPTION

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New compositions of this invention comprise copper-substituted alpha-chromium oxide containing from about 0.05 atom % to about 5 atom % copper based on the total of the copper and chromium in the alpha-chromium oxide which retains the corundum structure. This invention includes a catalytic composition comprising said crystalline copper-substituted $\alpha\text{-Cr}_2\text{O}_3$. The crystalline copper-substituted alpha-chromium oxides have the general formula $\alpha\text{-Cu}_x\text{Cr}_{2-x}\text{O}_3$ where $x = 0.001\text{-}0.10$. However, it is understood that inasmuch as the copper component of these crystalline oxides is generally divalent, the oxygen component may average slightly less than three atoms per formula unit in order to maintain charge neutrality (i.e., there is a small percentage of vacant oxygen sites). Of note are embodiments containing at least 1 atom % copper based on the total of the copper and chromium in the alpha-chromium oxide (e.g., from about 2 atom % to about 3 atom % copper based on the total of the copper and chromium in the alpha-chromium oxide).

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The compositions of the present invention may be prepared by co-precipitation. In the typical co-precipitation technique, an aqueous solution of copper(II) salts and chromium(III) salts is prepared. The relative concentrations of copper and chromium salts in the aqueous solution is dictated by the bulk atom percent copper relative to chromium desired in the final catalyst. The concentration of chromium salt in the aqueous solution is typically in the range of from about 0.3 to about 3 molar (moles per liter) with about 0.75-1.5 molar being a preferred concentration. Chromium(III) salts suitable for preparation of the aqueous solution are the

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nitrate, sulfate, acetate, formate, oxalate, phosphate, bromide, and chloride and various hydrated forms of these salts. Other chromium(III) salts that are useful for the preparation of the aqueous solutions include hexacoordinate complexes of the formula $[\text{CrL}_{6-z}\text{A}_z]^{+3-z}$ where each L is a neutral (i.e., uncharged) ligand selected from the group consisting of H_2O , NH_3 , $\text{C}_1\text{-C}_4$ primary, secondary, or tertiary organic amines, a $\text{C}_1\text{-C}_4$ alkyl nitriles, or pyridine, where each A is an anionic ligand selected from the group consisting of fluoride, chloride, bromide, iodide, hydroxide, nitrite, and nitrate, and where z has a value of from 0 to 3 inclusive. Included are neutral bidentate ligands such as ethylene diamine which are equivalent to two L in that they may occupy two coordination sites. Also included are anionic bidentate ligands such as $\text{C}_1\text{-C}_4$ carboxylate which may occupy two coordination sites. Also included are dianionic ligands such as sulfate which are equivalent to two A ligands and may occupy more than one coordination site.

Chromium(VI) precursors, such as CrO_3 , though not preferred, may be used but require reduction to Cr(III) with a compound such as ethanol before precipitation.

Chromium(III) nitrate, or its hydrated forms such as $[\text{Cr}(\text{NO}_3)_3(\text{H}_2\text{O})_9]$, are the most preferred chromium(III) salt for preparation of said aqueous solution.

Copper(II) salts suitable for preparation of the aqueous solution are the nitrate, sulfate, formate, oxalate, bromide, and chloride and various hydrated forms of these salts. Copper(II) nitrate hydrate (e.g., $[\text{Cu}(\text{NO}_3)_2(\text{H}_2\text{O})_{2.5}]$) is the most preferred copper(II) salt.

Of note are embodiments wherein the soluble copper and chromium salts are nitrates or hydrated nitrates.

The aqueous solution of the copper salts and chromium(III) salts is then treated with a base such as ammonium hydroxide (aqueous ammonia) to precipitate copper and chromium as the hydroxides. The addition of ammonium hydroxide to the aqueous solution of copper and chromium(III) salts is typically carried out gradually over a period of 1 to 12 hours. The pH of the solution is monitored during the addition of base. The final pH is typically in the range of 6.0 to 11.0, preferably from about 7.5 to about 9.0, and most preferably from about 8.0 to 8.7. The precipitation of the copper hydroxide/chromium hydroxide mixture is typically carried out at a temperature of about 15°C to about 60°C ,

preferably from about 20°C to about 40°C. After the ammonium hydroxide is added, the mixture is typically stirred for up to 24 hours.

Optionally, excess ammonium nitrate (i.e., more than three moles of ammonium nitrate per mole of chromium) may be added to the aqueous solution. For example, in addition to the ammonium nitrate already present from reaction of ammonium hydroxide with chromium nitrate, from about 0.1 mole to about 7.0 moles of additional ammonium nitrate per mole of chromium may be added to the solution before, during, or after the co-precipitation of the compositions.

After the ammonium nitrate is added to the mixture, it is preferably stirred for about 0.5 to ten hours (preferably for about one to five hours) at a temperature of from about 20°C to about 60°C. The mixture is then dried and calcined as indicated below.

Other agents that serve this purpose include aqueous hydrogen peroxide (1% to 30% solutions), ozone, peroxy acids such as peroxyacetic acid, and ammonium persulfate. Agents such as halogens may be used but are not preferred. Agents containing alkali metals such as potassium persulfate or sodium perborate may also be used, but are not preferred.

After the precipitation of the mixture of copper and chromium hydroxides is complete, and the ammonium nitrate or other agents added if desired, the mixture is dried by evaporation.

After the copper and chromium hydroxide mixture has been dried, the residual nitrate salts are then decomposed by heating the solid from about 250°C to about 350°C. The resulting solid is then calcined at temperature of from about 375°C to about 1000°C, preferably from about 400°C to about 900°C. The calcination is preferably carried out in the presence of oxygen, most preferably in the presence of air.

Compositions of this invention may also be prepared by a thermal method. In this method, a solution of the copper and chromium(III) salt is prepared as described for the co-precipitation technique. The mixed solution of the salts is then evaporated under atmospheric pressure or reduced pressure to give a solid. The solid is then placed in a furnace and the temperature raised gradually to decompose the salt. It is preferred to use the nitrate salts that decompose to the oxide. After decomposition of the nitrate salts is complete (about 350°C), the increase in temperature is continued until the desired calcination temperature is reached. The desired calcination temperature is between about 450°C to about 1000°C, a temperature of about 450°C to about 900°C being preferred. After the

desired calcination temperature is reached, the solid is maintained at this temperature for an additional 8 to 24 hours, about 8 to about 12 hours being preferred. The decomposition and calcination is preferably carried out in the presence of oxygen, most preferably in the presence of air.

5 The metal oxide compositions of this invention may be characterized by well-established analytical techniques including X-Ray absorption spectroscopy (XAS), X-ray powder diffraction (XRD), transmission electron microscopy (TEM), and energy dispersive spectroscopy (EDS). EDS is an analytical tool available in conjunction
10 with scanning or analytical TEM.

After calcination, the resulting copper-substituted crystallites are not visually distinguishable from α -Cr₂O₃ by TEM. Furthermore, X-ray and electron diffraction studies are entirely consistent with the α -Cr₂O₃ structure with some change in the lattice constants due to Cu(II)
15 substituting for Cr(III) in the structure. The compositions are therefore concluded to have the general formula Cu_xCr_{2-x}O₃ where x = 0.001-0.10. The EDS analysis from a sample containing 2 atom % Cu shows a uniform presence of Cu throughout the chromia particles, whereas this signal is absent in the chromia particles of a control sample when it is similarly
20 analyzed.

XAS and XRD data were obtained for compositions that were nominally 100% Cr (no copper added), Cr99%/Cu1%, and Cr98%/Cu2%. XAS and XRD analysis clearly show that copper is substituted into α -Cr₂O₃. XRD results for Cr98%/Cu2% are shown in Table A (the numbers
25 in the parentheses represent the standard deviations associated with the respective determinations). Diffraction peaks having d-spacings of 3.1335, 1.9188, and 1.6373 are due to a silicon internal standard added to the sample for calibration of the diffractometer. The peak at 1.7814 is due to the diffractometer sample holder. All other diffraction peaks can be
30 indexed to the α -Cr₂O₃ structure with small adjustments to the lattice constants.

TABLE A
XRD Results for a Cu-Substituted α -Cr₂O₃ Composition
that is Nominally 98 atom % Cr/2 atom % Cu

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D (Angstroms)	Height	FWHM a.
3.6300(0.0027)	179(3)	0.482(0.009)
3.1335(0.0011)	73(4)	0.115(0.010)
2.6656(0.0010)	354(4)	0.440(0.006)
2.4780(0.0004)	610(9)	0.237(0.003)
2.2608(0.0018)	40(2)	0.247(0.021)
2.1731(0.0005)	226(6)	0.234(0.006)
2.0571(0.0006)	123(5)	0.207(0.011)
1.9188(0.0004)	51(4)	0.108(0.012)
1.8159(0.0011)	111(2)	0.553(0.014)
1.7814(0.0011)	26(3)	0.232(0.038)
1.6714(0.0002)	526(8)	0.304(0.004)
1.6373(0.0003)	69(4)	0.107(0.010)
1.5793(0.0021)	22(1)	0.607(0.050)

a. FWHM means full width at half maximum.

If Cu(II) substitutes for Cr(III) in the α -Cr₂O₃ phase, it is expected to be in a distorted octahedral coordination environment. We do not expect Cu²⁺ to be found in a regular octahedral environment with 6 equal length Cu-O bonds, because of the Jahn-Teller distortion of the valence orbitals. XAS results from the Cr-K edge of the samples indicate that all Cr is present as Cr³⁺ and is octahedrally coordinated.

Figure 1 shows the radial distribution function (RDF) for five materials. The radial distribution function represents the probability of finding an atom at a certain distance, r , from a central atom. These probabilities are weighted by factors that depend on the type of atom. Thus an RDF is a representation of local atomic structure around the central atom. An RDF is obtained by Fourier transform of the extended x-ray absorption fine structure (EXAFS) data, and may be represented by a plot of the dimensionless Fourier transform magnitude, F , versus the pair separation distance in angstroms. In simplified terms, one might view a

peak in an RDF plot as indicative of a distance at which there is a coordination sphere around the central atom. A small difference is expected between the actual separation distance and the "r" shown in a plot when no correction is made to account for the phase shift on backscattering of excited electrons. In Figure 1, F is plotted against the pair separation distance, r (shown in angstroms, uncorrected for phase shift) for each of the five materials. Included in Figure 1 are curve A representing the local structure around copper in Cu_2O , curve B representing the local structure around copper in CuO , curve C representing the local structure around copper in $\text{Cu}_2\text{Cr}_2\text{O}_5$, curve D representing the local structure around chromium in $\alpha\text{-Cr}_2\text{O}_3$. Also included in Figure 1 is curve E representing the local structure around copper in the copper-substituted alpha-chromium oxide with a nominal composition of 99% chromium and 1% copper, and curve F representing the local structure around copper in the copper-substituted alpha-chromium oxide with a nominal composition of 98% chromium and 2% copper. XAS near edge spectroscopy indicates Cu is present as Cu^{2+} in the copper-substituted alpha-chromium oxides, so cuprous chromium oxides need not be considered. The curves (E & F) in Figure 1 representing the local structure around copper in the copper-substituted alpha-chromium oxides, indicate that the local atomic structure around Cu in these samples bears no resemblance to that of expected common copper oxide phases, or known mixed Cr-Cu oxides, rather it is very similar to that of Cr in the $\alpha\text{-Cr}_2\text{O}_3$ phase with distortions due to the distorted Cu^{2+} valence electron structure. These distortions manifest themselves in the observed lattice constants for the copper-substituted-chromia phase.

The calcined chromium oxide compositions of the present invention may be formed into various shapes such as pellets, granules, and extrudates for use in packing reactors. It may also be used in powder form.

The compositions of this invention may further comprise one or more additives in the form of metal compounds that alter the selectivity or activity of the crystalline copper-substituted alpha-chromium oxides or the fluorinated metal oxide catalysts containing copper and chromium. Suitable additives may be selected from the group consisting of fluorides, oxides, or oxyfluoride compounds of Mg, Ca, Sc, Y, La, Ti, Zr, Hf, V, Nb, Ta, Mo, W, Mn, Re, Fe, Ru, Co, Rh, Ir, Ni, Pd, Pt, Ag, Au, Ce, and Zn.

The total content of the additive(s) in the compositions of the present invention may be from about 0.05 atom % to about 15 atom % based on the total metal content of the compositions. The additives may be incorporated into the compositions of the present invention by standard
5 procedures such as by impregnation.

Typically, the calcined compositions will be pre-treated with a fluorinating agent prior to use as catalysts for changing the fluorine distribution of hydrocarbons and/or halogenated hydrocarbon compounds. Typically this fluorinating agent is HF though other materials may be used
10 such sulfur tetrafluoride, carbonyl fluoride, and fluorinated hydrocarbon compounds such as trichlorofluoromethane, dichlorodifluoromethane, chlorodifluoromethane, trifluoromethane, or 1,1,2-trichlorotrifluoroethane. This pretreatment can be accomplished, for example, by placing the catalyst in a suitable container which can be the reactor to be used to
15 perform the process in the instant invention, and thereafter, passing HF over the dried, calcined catalyst so as to partially saturate the catalyst with HF. This is conveniently carried out by passing HF over the catalyst for a period of time, for example, about 0.1 to about 10 hours at a temperature of, for example, about 200°C to about 450°C. Nevertheless, this pre-
20 treatment is not essential.

As noted above catalysts provided in accordance with this invention may be used for changing the fluorine distribution in hydrocarbons and/or halogenated hydrocarbons. The fluorine distribution in a hydrocarbon or a halogenated hydrocarbon may be changed by increasing the fluorine
25 content of the hydrocarbon or the halogenated hydrocarbon. The fluorine distribution of a halogenated hydrocarbon may also be changed by decreasing the fluorine content of the halogenated hydrocarbon and/or rearranging the placement of fluorine atoms on the carbon atoms of the halogenated hydrocarbon. Of note are processes where the fluorine
30 distribution in halogenated hydrocarbons containing from one to twelve carbon atoms is changed, particularly processes where the fluorine distribution in halogenated hydrocarbons containing from one to six carbon atoms is changed. Also of note are processes where the fluorine content of hydrocarbons containing from one to twelve carbon atoms is increased,
35 particularly processes where the fluorine content in hydrocarbons containing one to six carbon atoms is increased. Processes for changing the fluorine distribution in halogenated hydrocarbons include fluorination, chlorofluorination, isomerization, disproportionation, dehydrofluorination

and chlorodefluorination. The processes of this invention are characterized by using as the catalyst a composition comprising at least one chromium-containing component selected from the group consisting of the crystalline copper-substituted alpha-chromium oxide described above and said copper-substituted alpha-chromium oxide which has been
 5 treated with a fluorinating agent.

Typical of saturated halogenated hydrocarbons suitable for fluorination, chlorofluorination, isomerization, disproportionation, dehydrofluorination and chlorodefluorination processes are those which
 10 have the formula $C_nH_aBr_bCl_cF_d$, wherein n is an integer from 1 to 6, a is an integer from 0 to 12, b is an integer from 0 to 4, c is an integer from 0 to 13, d is an integer from 0 to 13, the sum of b, c and d is at least 1 and the sum of a, b, c, and d is equal to $2n + 2$, provided that n is at least 2 for isomerization, disproportionation and dehydrofluorination processes, a is
 15 at least one for dehydrofluorination processes, b is 0 for chlorodefluorination processes, b + c is at least 1 for fluorination processes and is 0 for dehydrofluorination processes, a + b + c is at least 1 for fluorination, chlorofluorination, isomerization, disproportionation and dehydrofluorination processes and d is at least 1 for isomerization,
 20 disproportionation, dehydrofluorination and chlorodefluorination processes. Typical of unsaturated halogenated hydrocarbons suitable for fluorination, chlorofluorination, isomerization, disproportionation, and chlorodefluorination processes are those which have the formula $C_pH_eBr_fCl_gF_h$, wherein p is an integer from 2 to 6, e is an integer from 0 to
 25 10, f is an integer from 0 to 2, g is an integer from 0 to 12, h is an integer from 0 to 11, the sum of f, g and h is at least 1 and the sum of e, f, g, and h is equal to $2p$, provided that f is 0 for chlorodefluorination processes, e + f + g is at least 1 for isomerization and disproportionation processes and h is at least 1 for isomerization, disproportionation and chlorodefluorination
 30 processes. Typical of saturated hydrocarbons suitable for chlorofluorination are those which have the formula C_qH_r where q is an integer from 1 to 6 and r is $2q + 2$. Typical of unsaturated hydrocarbons suitable for fluorination and chlorofluorination are those which have the formula C_iH_j where i is an integer from 2 to 6 and j is $2i$.

35 Fluorination

Included in this invention is a process for increasing the fluorine content of a halogenated hydrocarbon compound or an unsaturated hydrocarbon compound by reacting said compound with hydrogen fluoride

in the vapor phase in the presence of a catalyst composition comprising at least one chromium-containing component selected from the group consisting of the crystalline copper-substituted alpha-chromium oxide described above and said copper-substituted alpha-chromium oxide which
5 has been treated with a fluorinating agent. The catalyst composition may optionally contain additional components such as additives to alter the activity and selectivity of the catalyst.

Halogenated hydrocarbon compounds suitable as starting materials for the fluorination process of this invention may be saturated or
10 unsaturated. Saturated halogenated hydrocarbon compounds suitable for the fluorination processes of this invention include those of the general formula $C_nH_aBr_bCl_cF_d$, wherein n is an integer from 1 to 6, a is an integer from 0 to 12, b is an integer from 0 to 4, c is an integer from 0 to 13, d is an integer from 0 to 13, and the sum of a, b, c, and d is equal to $2n + 2$,
15 provided that $b + c$ is at least 1. Unsaturated halogenated hydrocarbon compounds suitable for the fluorination processes of this invention include those of the general formula $C_pH_eBr_fCl_gF_h$, wherein p is an integer from 2 to 6, e is an integer from 0 to 10, f is an integer from 0 to 2, g is an integer from 0 to 12, h is an integer from 0 to 11, the sum of f, g and h is at least 1
20 and the sum of e, f, g, and h is equal to $2p$. Unsaturated hydrocarbons suitable for fluorination are those which have the formula C_iH_j where i is an integer from 2 to 6 and j is $2i$. The fluorine content of saturated compounds of the formula $C_nH_aBr_bCl_cF_d$, unsaturated compounds of the formula $C_pH_eBr_fCl_gF_h$ and/or unsaturated compounds of the formula C_iH_j
25 may be increased by reacting said compounds with HF in the vapor phase in the presence of a catalyst composition comprising at least one chromium-containing component selected from the group consisting of the crystalline copper-substituted alpha-chromium oxide described above and said copper-substituted alpha-chromium oxide which has been treated
30 with a fluorinating agent. Such a process is referred to herein as a vapor phase fluorination reaction.

The vapor phase fluorination reactions are typically conducted at temperatures of from about 150°C to 500°C. For saturated compounds the fluorination is preferably carried out from about 175°C to 400°C and
35 more preferably from about 200°C to about 350°C. For unsaturated compounds the fluorination is preferably carried out from about 150°C to 350°C and more preferably from about 175°C to about 300°C.

The vapor phase fluorination reactions are typically conducted at atmospheric and superatmospheric pressures. For reasons of convenience in downstream separations processes (e.g., distillation), pressures of up to about 30 atmospheres may be employed.

5 The vapor phase fluorination reactions are typically conducted in a tubular reactor. The reactor and its associated feed lines, effluent lines, and associated units should be constructed of materials resistant to hydrogen fluoride and hydrogen chloride. Typical materials of construction, well-known to the fluorination art, include stainless steels, in particular of the austenitic type, the well-known high nickel alloys, such as
10 Monel® nickel-copper alloys, Hastelloy® nickel-based alloys and, Inconel® nickel-chromium alloys, and copper-clad steel.

The contact time in the reactor is typically from about 1 to about 120 seconds. Of note are contact times of from about 5 to about
15 60 seconds.

The amount of HF reacted with the unsaturated hydrocarbons or halogenated hydrocarbon compounds should be at least a stoichiometric amount. The stoichiometric amount is based on the number of Br and/or Cl substituents to be replaced by F in addition to one mole of HF to
20 saturate the carbon-carbon double bond if present. Typically, the molar ratio of HF to the said compounds of the formulas $C_nH_aBr_bCl_cF_d$, $C_pH_eBr_fCl_gF_h$, and C_iH_j can range from about 0.5:1 to about 100:1, preferably from about 2:1 to about 50:1, and more preferably from about 3:1 to about 20:1. In general, with a given catalyst composition, the higher
25 the temperature and the longer the contact time, the greater is the conversion to fluorinated products. The above variables can be balanced, one against the other, so that the formation of higher fluorine substituted products is maximized.

Examples of saturated compounds of the formula $C_nH_aBr_bCl_cF_d$ which may be reacted with HF in the presence of the catalyst of this invention include CH_2Cl_2 , CH_2Br_2 , $CHCl_3$, CCl_4 , C_2Cl_6 , C_2BrCl_5 , C_2Cl_5F ,
30 $C_2Cl_4F_2$, $C_2Cl_3F_3$, $C_2Cl_2F_4$, C_2ClF_5 , C_2HCl_5 , C_2HCl_4F , $C_2HCl_3F_2$, $C_2HCl_2F_3$, C_2HClF_4 , C_2HBrF_4 , $C_2H_2Cl_4$, $C_2H_2Cl_3F$, $C_2H_2Cl_2F_2$, $C_2H_2ClF_3$, $C_2H_3Cl_3$, $C_2H_3Cl_2F$, $C_2H_3ClF_2$, $C_2H_4Cl_2$, C_2H_4ClF , $C_3Cl_6F_2$,
35 $C_3Cl_5F_3$, $C_3Cl_4F_4$, $C_3Cl_3F_5$, C_3HCl_7 , C_3HCl_6F , $C_3HCl_5F_2$, $C_3HCl_4F_3$, $C_3HCl_3F_4$, $C_3HCl_2F_5$, $C_3H_2Cl_6$, $C_3H_2BrCl_5$, $C_3H_2Cl_5F$, $C_3H_2Cl_4F_2$, $C_3H_2Cl_3F_3$, $C_3H_2Cl_2F_4$, $C_3H_2ClF_5$, $C_3H_3Cl_5$, $C_3H_3Cl_4F$, $C_3H_3Cl_3F_2$,

$C_3H_3Cl_2F_3$, $C_3H_3ClF_4$, $C_3H_4Cl_4$, $C_4Cl_4Cl_4$, $C_4Cl_4Cl_6$, $C_4H_5Cl_5$, $C_4H_5Cl_4F$, and $C_5H_4Cl_8$.

Specific examples of fluorination reactions of saturated halogenated hydrocarbon compounds which may be carried out under the conditions described above using the catalysts of this invention include the

5 conversion of CH_2Cl_2 to CH_2F_2 , the conversion of $CHCl_3$ to a mixture of $CHCl_2F$, $CHClF_2$, and CHF_3 , the conversion of CH_3CHCl_2 to a mixture of CH_3CHClF and CH_3CHF_2 , the conversion of CH_2ClCH_2Cl to a mixture of CH_3CHClF and CH_3CHF_2 , the conversion of CH_3CCl_3 to a mixture of

10 CH_3CCl_2F , CH_3CClF_2 , and CH_3CF_3 , the conversion of CH_2ClCF_3 to CH_2FCF_3 , the conversion of $CHCl_2CF_3$ to a mixture of $CHClFCF_3$ and CHF_2CF_3 , the conversion of $CHClFCF_3$ to CHF_2CF_3 , the conversion of $CHBrFCF_3$ to CHF_2CF_3 , the conversion of $CCl_3CF_2CCl_3$ to a mixture of $CCl_2FCF_2CClF_2$ and $CClF_2CF_2CClF_2$, the conversion of $CCl_3CH_2CCl_3$ to

15 $CF_3CH_2CClF_2$ and $CF_3CH_2CF_3$, the conversion of $CCl_3CH_2CHCl_2$ to a mixture of $CF_3CH_2CHF_2$, $CF_3CH=CHCl$, and $CF_3CH=CHF$, the conversion of $CF_3CCl_2CClF_2$ to a mixture of $CF_3CCl_2CF_3$, and $CF_3CClFCF_3$, the conversion of $CF_3CCl_2CF_3$ to CF_3ClFCF_3 , and the conversion of a mixture comprising $CF_3CF_2CHCl_2$ and $CClF_2CF_2CHClF$ to

20 a mixture of CF_3CF_2CHClF and $CF_3CF_2CHF_2$.

Examples of unsaturated compounds of the formula $C_pH_eBr_fCl_gF_h$ and C_iH_j which may be reacted with HF in the presence of the catalysts of this invention include C_2Cl_4 , C_2BrCl_3 , C_2Cl_3F , $C_2Cl_2F_2$, C_2ClF_3 , C_2F_4 , C_2HCl_3 , C_2HBrCl_2 , C_2HCl_2F , C_2HClF_2 , C_2HF_3 , $C_2H_2Cl_2$, C_2H_2ClF ,

25 $C_2H_2F_2$, C_2H_3Cl , C_2H_3F , C_2H_4 , C_3H_6 , C_3H_5Cl , $C_3H_4Cl_2$, $C_3H_3Cl_3$, $C_3H_2Cl_4$, C_3HCl_5 , C_3Cl_6 , C_3Cl_5F , $C_3Cl_4F_2$, $C_3Cl_3F_3$, $C_3Cl_2F_4$, C_3ClF_5 , C_3HF_5 , $C_3H_2F_4$, C_3F_6 , C_4Cl_8 , $C_4Cl_2F_6$, C_4ClF_7 , $C_4H_2F_6$, and C_4HClF_6 .

Specific examples of fluorination reactions of unsaturated halogenated hydrocarbon compounds which may be carried out using the

30 catalysts of this invention include the conversion of $CHCl=CCl_2$ to a mixture of CH_2ClCF_3 and CH_2FCF_3 , the conversion of $CCl_2=CCl_2$ to a mixture of $CHCl_2CF_3$, $CHClFCF_3$, and CHF_2CF_3 , the conversion of $CCl_2=CH_2$ to a mixture of CH_3CCl_2F , CH_3CClF_2 , and CH_3CF_3 , the conversion of $CH_2=CHCl$ to a mixture of CH_3CHClF and CH_3CHF_2 , the

35 conversion of $CF_2=CH_2$ to CH_3CF_3 , the conversion of $CCl_2=CClCF_3$ to a mixture of $CF_3CHClCClF_2$, $CF_3CHClCF_3$, and/or $CF_3CCl=CF_2$, the conversion of $CF_3CF=CF_2$ to CF_3CHFCF_3 , the conversion of $CF_3CH=CF_2$ to $CF_3CH_2CF_3$, and the conversion of $CF_3CH=CHF$ to $CF_3CH_2CHF_2$.

Of note is a catalytic process for producing a mixture of 2-chloro-1,1,1,3,3,3-hexafluoropropene (i.e., $\text{CF}_3\text{CHClCF}_3$ or HCFC-226da) and 2-chloro-pentafluoropropene (i.e., $\text{CF}_3\text{CCl}=\text{CF}_2$ or CFC-1215xc) by the fluorination of a hexahalopropene of the formula $\text{C}_3\text{Cl}_{6-x}\text{F}_x$, wherein x equals 0 to 4. Preferred hexahalopropenes of the formula $\text{C}_3\text{Cl}_{6-x}\text{F}_x$ include 1,1,2-trichloro-3,3,3-trifluoro-1-propene (i.e., $\text{CCl}_2=\text{CClCF}_3$ or CFC-1213xa) and hexachloropropene (i.e., $\text{CCl}_2=\text{CClCCl}_3$). The mixture of HCFC-226da and CFC-1215xc is produced by reacting the above unsaturated compounds with HF in the vapor phase in the presence of the catalysts of this invention at temperatures from about 150°C to about 400°C, preferably about 200°C to about 350°C.

The amount of HF fed to the reactor should be at least a stoichiometric amount based on the number of Cl substituents in the $\text{C}_3\text{Cl}_{6-x}\text{F}_x$ starting material(s). In the case of fluorination of CFC-1213xa, the stoichiometric ratio of HF to CFC-1213xa is 3:1. Preferred ratios of HF to $\text{C}_3\text{Cl}_{6-x}\text{F}_x$ starting material(s) are typically in the range of about the stoichiometric ratio to about 25:1. Preferred contact times are typically in the range of from 1 to 60 seconds.

Further information on the fluorination of CFC-1213xa is provided in U.S. Patent Application 60/706,164 filed August 5, 2005, and hereby incorporated by reference herein in its entirety.

Mixtures of saturated halogenated hydrocarbon compounds or mixtures of unsaturated hydrocarbons and/or halogenated hydrocarbon compounds may also be used in the vapor phase fluorination reactions as well as mixtures comprising both unsaturated hydrocarbons and halogenated hydrocarbon compounds. Specific examples of mixtures of saturated halogenated hydrocarbon compounds and mixtures of unsaturated hydrocarbons and unsaturated halogenated hydrocarbon compounds that may be subjected to vapor phase fluorination using the catalysts of this invention include a mixture of CH_2Cl_2 and $\text{CCl}_2=\text{CCl}_2$, a mixture of $\text{CCl}_2\text{FCClF}_2$ and CCl_3CF_3 , a mixture of $\text{CCl}_2=\text{CCl}_2$ and $\text{CCl}_2=\text{CClCCl}_3$, a mixture of $\text{CH}_2=\text{CHCH}_3$ and $\text{CH}_2=\text{CClCH}_3$, a mixture of CH_2Cl_2 and CH_3CCl_3 , a mixture of $\text{CHF}_2\text{CClF}_2$ and CHClFCF_3 , a mixture of $\text{CHCl}_2\text{CCl}_2\text{CH}_2\text{Cl}$ and $\text{CCl}_3\text{CHClCH}_2\text{Cl}$, a mixture of $\text{CHCl}_2\text{CH}_2\text{CCl}_3$ and $\text{CCl}_3\text{CHClCH}_2\text{Cl}$, a mixture of $\text{CHCl}_2\text{CHClCCl}_3$, $\text{CCl}_3\text{CH}_2\text{CCl}_3$, and $\text{CCl}_3\text{CCl}_2\text{CH}_2\text{Cl}$, a mixture of $\text{CHCl}_2\text{CH}_2\text{CCl}_3$ and $\text{CCl}_3\text{CH}_2\text{CCl}_3$, a mixture of and $\text{CF}_3\text{CH}_2\text{CCl}_2\text{F}$ and $\text{CF}_3\text{CH}=\text{CCl}_2$, and a mixture of $\text{CF}_3\text{CH}=\text{CHCl}$ and $\text{CF}_3\text{CH}=\text{CCl}_2$.

Chlorofluorination

Included in this invention is a process for increasing the fluorine content of a halogenated hydrocarbon compound or a hydrocarbon compound by reacting said compound with hydrogen fluoride (HF) and chlorine (Cl_2) in the vapor phase in the presence of a catalyst composition comprising at least one chromium-containing component selected from the group consisting of the crystalline copper-substituted alpha-chromium oxide described above and said copper-substituted alpha-chromium oxide which has been treated with a fluorinating agent. The catalyst composition may optionally contain additional components such as another catalytically effective metal.

Halogenated hydrocarbon compounds suitable as starting materials for the chlorofluorination process of this invention may be saturated or unsaturated. Saturated halogenated hydrocarbon compounds suitable for the chlorofluorination processes of this invention include those of the general formula $\text{C}_n\text{H}_a\text{Br}_b\text{Cl}_c\text{F}_d$, wherein n is an integer from 1 to 6, a is an integer from 0 to 12, b is an integer from 0 to 4, c is an integer from 0 to 13, d is an integer from 0 to 13, the sum of b , c and d is at least 1 and the sum of a , b , c , and d is equal to $2n + 2$, provided that $a + b + c$ is at least 1. Preferred chlorofluorination processes include those involving said saturated starting materials where a is at least 1. Saturated hydrocarbon compounds suitable for chlorofluorination are those which have the formula C_qH_r where q is an integer from 1 to 6 and r is $2q + 2$. Unsaturated halogenated hydrocarbon compounds suitable for the chlorofluorination processes of this invention include those of the general formula $\text{C}_p\text{H}_e\text{Br}_f\text{Cl}_g\text{F}_h$, wherein p is an integer from 2 to 6, e is an integer from 0 to 10, f is an integer from 0 to 2, g is an integer from 0 to 12, h is an integer from 0 to 11, the sum of f , g and h is at least 1 and the sum of e , f , g , and h is equal to $2p$. Unsaturated hydrocarbon compounds suitable for fluorination are those which have the formula C_iH_j where i is an integer from 2 to 6 and j is $2i$. The fluorine content of saturated compounds of the formula $\text{C}_n\text{H}_a\text{Br}_b\text{Cl}_c\text{F}_d$ and C_qH_r and/or unsaturated compounds of the formula $\text{C}_p\text{H}_e\text{Br}_f\text{Cl}_g\text{F}_h$ and C_iH_j may be increased by reacting said compounds with HF and Cl_2 in the vapor phase in the presence of a catalyst composition comprising at least one chromium-containing component selected from the group consisting of the crystalline copper-substituted alpha-chromium oxide described above and said copper-substituted alpha-chromium oxide which has been treated with a

fluorinating agent. Such a process is referred to herein as a vapor phase chlorofluorination reaction.

The conditions of the vapor phase chlorofluorination reactions are similar to those described above for vapor phase fluorination reactions in terms of the temperature ranges, contact times, pressures, and mole ratios of HF to the halogenated hydrocarbon compounds. The amount of chlorine (Cl_2) fed to the reactor is based on whether the halogenated hydrocarbon compounds fed to the reactor is unsaturated and the number of hydrogens in $\text{C}_n\text{H}_a\text{Br}_b\text{Cl}_c\text{F}_d$, C_qH_r , $\text{C}_p\text{H}_e\text{Br}_f\text{Cl}_g\text{F}_h$, and C_iH_j that are to be replaced by chlorine and fluorine. One mole of Cl_2 is required to saturate a carbon-carbon double bond and a mole of Cl_2 is required for every hydrogen to be replaced by chlorine or fluorine. A slight excess of chlorine over the stoichiometric amount may be necessary for practical reasons, but large excesses of chlorine will result in complete chlorofluorination of the products. The ratio of Cl_2 to halogenated carbon compound is typically from about 1:1 to about 10:1.

Specific examples of vapor phase chlorofluorination reactions of saturated halogenated hydrocarbon compounds of the general formula $\text{C}_n\text{H}_a\text{Br}_b\text{Cl}_c\text{F}_d$ and saturated hydrocarbon compounds of the general formula C_qH_r which may be carried out using the catalysts of this invention include the conversion of C_2H_6 to a mixture containing CH_2ClCF_3 , the conversion of CH_2ClCF_3 to a mixture of CHClFCF_3 and CHF_2CF_3 , the conversion of $\text{CCl}_3\text{CH}_2\text{CH}_2\text{Cl}$ to a mixture of $\text{CF}_3\text{CCl}_2\text{CClF}_2$, $\text{CF}_3\text{CCl}_2\text{CF}_3$, $\text{CF}_3\text{CClFCClF}_2$, and $\text{CF}_3\text{CClFCF}_3$, the conversion of $\text{CCl}_3\text{CH}_2\text{CHCl}_2$ to a mixture of $\text{CF}_3\text{CCl}_2\text{CClF}_2$, $\text{CF}_3\text{CCl}_2\text{CF}_3$, $\text{CF}_3\text{CClFCClF}_2$, and $\text{CF}_3\text{CClFCF}_3$, the conversion of $\text{CCl}_3\text{CHClCH}_2\text{Cl}$ to a mixture of $\text{CF}_3\text{CCl}_2\text{CClF}_2$, $\text{CF}_3\text{CCl}_2\text{CF}_3$, $\text{CF}_3\text{CClFCClF}_2$, and $\text{CF}_3\text{CClFCF}_3$, the conversion of $\text{CHCl}_2\text{CCl}_2\text{CH}_2\text{Cl}$ to a mixture of $\text{CF}_3\text{CCl}_2\text{CClF}_2$, $\text{CF}_3\text{CCl}_2\text{CF}_3$, $\text{CF}_3\text{CClFCClF}_2$, and $\text{CF}_3\text{CClFCF}_3$, the conversion of $\text{CCl}_3\text{CH}_2\text{CH}_2\text{Cl}$ to a mixture of $\text{CF}_3\text{CCl}_2\text{CHF}_2$, $\text{CF}_3\text{CClFCHF}_2$, $\text{CF}_3\text{CClFCClF}_2$, and $\text{CF}_3\text{CCl}_2\text{CF}_3$, and the conversion of $\text{CCl}_3\text{CH}_2\text{CHCl}_2$ to a mixture of $\text{CF}_3\text{CCl}_2\text{CHF}_2$, $\text{CF}_3\text{CClFCHF}_2$, $\text{CF}_3\text{CClFCClF}_2$, and $\text{CF}_3\text{CCl}_2\text{CF}_3$.

Specific examples of vapor phase chlorofluorination reactions of unsaturated halogenated hydrocarbon compounds of the general formula $\text{C}_p\text{H}_e\text{Br}_f\text{Cl}_g\text{F}_h$ and unsaturated hydrocarbon compounds of the general formula C_iH_j which may be carried out using the catalysts of this invention include the conversion of C_2H_4 to a mixture of $\text{CCl}_3\text{CClF}_2$, $\text{CCl}_2\text{FCCl}_2\text{F}$,

CClF₂CCl₂F, CCl₃CF₃, CF₃CCl₂F, and CClF₂CClF₂, the conversion of C₂Cl₄ to a mixture of CCl₃CClF₂, CCl₂FCCl₂F, CClF₂CCl₂F, CCl₃CF₃, CF₃CCl₂F, and CClF₂CClF₂, and the conversion of C₃H₆ or CF₃CCl=CCl₂ to a mixture of CF₃CCl₂CClF₂, CF₃CCl₂CF₃, CF₃CClFCClF₂, and

5 CF₃CClFCF₃.

Of note is a catalytic process for producing a mixture of 1,2,2-trichloro-1,1,3,3,3-pentafluoropropane (i.e., CClF₂CCl₂CF₃ or CFC-215aa), 1,1,2-trichloro-1,2,3,3,3-pentafluoropropane (i.e., CCl₂FCClFCF₃ or CFC-215bb), 2,2-dichloro-1,1,1,3,3,3-
 10 hexafluoropropane (i.e., CF₃CCl₂CF₃ or CFC-216aa), 1,2-dichloro-1,1,1,3,3,3-hexafluoropropane (i.e., CClF₂CClFCF₃ or CFC-216ba), and 2-chloro-1,1,1,2,3,3,3-heptafluoropropane (i.e., CF₃CClFCF₃ or CFC-217ba), by the chlorofluorination of a hexahalopropene of the formula C₃Cl_{6-x}F_x, wherein x equals 0 to 4. Preferred hexahalopropenes
 15 of the formula C₃Cl_{6-x}F_x include 1,1,2-trichloro-3,3,3-trifluoro-1-propene (i.e., CCl₂=CClCF₃ or CFC-1213xa) and hexachloropropene (i.e., CCl₂=CClCCl₃). The mixture of CFC-215aa, -215bb, -216aa, -216ba, and -217ba is produced by reacting the above unsaturated compounds with Cl₂ and HF in the vapor phase in the presence of the catalysts of this
 20 invention at temperatures from about 150°C to about 450°C, preferably about 250°C to 400°C.

The amount of HF fed to the reactor should be at least a stoichiometric amount based on the number of Cl substituents in the C₃Cl_{6-x}F_x starting material(s) and the desired composition of the final
 25 product. In the case of chlorofluorination of CFC-1213xa to a mixture of chlorofluoropropanes having an average number of fluorine substituents of six, the stoichiometric ratio of HF to CFC-1213xa is 3:1. Preferred ratios of HF to C₃Cl_{6-x}F_x starting material(s) are typically in the range of about the stoichiometric ratio to about 30:1, more preferably from about 8:1 to
 30 25:1.

The amount of chlorine fed to the reactor should be at least a stoichiometric amount. Preferred molar ratios of Cl₂ to CFC-1213xa are from about 1:1 to about 5:1.

Of note are contact times of from about 5 seconds to about
 35 60 seconds.

Further information on the chlorofluorination of CFC-1213xa is provided in U.S. Patent Applications 60/706,161 and 60/706,162 filed

August 5, 2005, and hereby incorporated by reference herein in their entirety.

Mixtures of saturated hydrocarbon compounds and saturated halogenated hydrocarbon compounds and mixtures of unsaturated hydrocarbon compounds and unsaturated halogenated hydrocarbon compounds as well as mixtures comprising both saturated and unsaturated compounds may be chlorofluorinated using the catalysts of the present invention. Specific examples of mixtures of saturated and unsaturated hydrocarbons and halogenated hydrocarbons that may be used include a mixture of $\text{CCl}_2=\text{CCl}_2$ and $\text{CCl}_2=\text{CClCCl}_3$, a mixture of $\text{CHCl}_2\text{CCl}_2\text{CH}_2\text{Cl}$ and $\text{CCl}_3\text{CHClCH}_2\text{Cl}$, a mixture of $\text{CHCl}_2\text{CH}_2\text{CCl}_3$ and $\text{CCl}_3\text{CHClCH}_2\text{Cl}$, a mixture of $\text{CHCl}_2\text{CHClCCl}_3$, $\text{CCl}_3\text{CH}_2\text{CCl}_3$, and $\text{CCl}_3\text{CCl}_2\text{CH}_2\text{Cl}$, a mixture of $\text{CHF}_2\text{CH}_2\text{CF}_3$ and $\text{CHCl}=\text{CHCF}_3$, and a mixture of $\text{CH}_2=\text{CH}_2$ and $\text{CH}_2=\text{CHCH}_3$.

15 Isomerization and Disproportionation

Included in this invention is a process for changing the fluorine distribution in a halogenated hydrocarbon compound by isomerizing said halogenated hydrocarbon compound in the presence of a catalyst composition comprising at least one chromium-containing component selected from the group consisting of the crystalline copper-substituted-chromium oxide described above and said copper-substituted alpha-chromium oxide which has been treated with a fluorinating agent.

Also included in this invention is a process for changing the fluorine distribution in a halogenated hydrocarbon compound by disproportionating said halogenated hydrocarbon compound in the vapor phase in the presence of a catalyst composition comprising at least one chromium-containing component selected from the group consisting of the crystalline copper-substituted alpha-chromium oxide described above and said copper-substituted alpha-chromium oxide which has been treated with a fluorinating agent.

Halogenated hydrocarbon compounds suitable as starting materials for the isomerization and disproportionation processes of this invention may be saturated or unsaturated. Saturated halogenated hydrocarbon compounds suitable for the isomerization and disproportionation processes of this invention include those of the general formula $\text{C}_n\text{H}_a\text{Br}_b\text{Cl}_c\text{F}_d$, wherein n is an integer from 2 to 6, a is an integer from 0 to 12, b is an integer from 0 to 4, c is an integer from 0 to 13, d is an integer from 1 to 13, and the sum of a , b , c , and d is equal to $2n + 2$, provided that

a + b + c is at least 1. Unsaturated halogenated hydrocarbon compounds suitable for the isomerization and disproportionation processes of this invention include those of the general formula $C_pH_eBr_fCl_gF_h$, wherein p is an integer from 2 to 6, e is an integer from 0 to 10, f is an integer from 0 to 2, g is an integer from 0 to 12, h is an integer from 1 to 11, and the sum of e, f, g, and h is equal to 2p, provided that the sum of e + f + g is at least 1.

In one embodiment of the present invention, the fluorine distribution of a halogenated hydrocarbon compound is changed by rearranging the H, Br, Cl, and F substituents in the molecule (typically to a thermodynamically preferred arrangement) while maintaining the same number of the H, Br, Cl, and F substituents, respectively. This process is referred to herein as isomerization.

In another embodiment of the present invention, the fluorine distribution of a halogenated hydrocarbon compound is changed by exchanging at least one F substituent of the halogenated hydrocarbon starting material with at least one H, Br and/or Cl substituent of another molecule of the halogenated hydrocarbon starting material so as to result in the formation of one or more halogenated hydrocarbon compounds having a decreased fluorine content compared to the halogenated hydrocarbon starting material and one or more halogenated hydrocarbon compounds having an increased fluorine content compared to the halogenated hydrocarbon starting material. This process is referred to herein as disproportionation.

In another embodiment of the present invention, both isomerization and disproportionation reactions may occur simultaneously.

Whether carrying out isomerization, disproportionation or both isomerization and disproportionation, the fluorine distribution of saturated compounds of the formula $C_nH_aBr_bCl_cF_d$ and/or unsaturated compounds of the formula $C_pH_eBr_fCl_gF_h$ may be changed in the presence of a catalyst composition comprising at least one chromium-containing component selected from the group consisting of the crystalline copper-substituted alpha-chromium oxide described above and said copper-substituted alpha-chromium oxide which has been treated with a fluorinating agent.

The isomerization and disproportionation reactions are typically conducted at temperatures of from about 150°C to 500°C, preferably from about 200°C to about 400°C. The contact time in the reactor is typically from about 1 to about 120 seconds and preferably from about 5 to about 60 seconds. The isomerization and disproportionation reactions may be

carried out in the presence of an inert gas such as helium, argon, or nitrogen though this is not preferred. The isomerization and disproportionation reactions may be carried out in the presence of HF and HCl, but this is not preferred.

- 5 Specific examples of vapor phase isomerization reactions which may be carried out using the catalysts of this invention include the conversion of $\text{CClF}_2\text{CCl}_2\text{F}$ to CCl_3CF_3 , the conversion of $\text{CClF}_2\text{CClF}_2$ to $\text{CF}_3\text{CCl}_2\text{F}$, the conversion of $\text{CHF}_2\text{CClF}_2$ to CF_3CHClF , the conversion of CHF_2CHF_2 to $\text{CF}_3\text{CH}_2\text{F}$, the conversion of $\text{CF}_3\text{CClFCClF}_2$ to $\text{CF}_3\text{CCl}_2\text{CF}_3$, and the conversion of $\text{CF}_3\text{CHFCHF}_2$ to $\text{CF}_3\text{CH}_2\text{CF}_3$.

- 10 Specific examples of vapor phase disproportionation reactions which may be carried out using the catalysts of this invention include the conversion of $\text{CClF}_2\text{CClF}_2$ to a mixture of $\text{CClF}_2\text{CCl}_2\text{F}$, CCl_3CF_3 , and CF_3CClF_2 , and the conversion of $\text{CHClF}_2\text{CF}_3$ to a mixture of CHCl_2CF_3 , and CHF_2CF_3 .

- 15 Of note is a process for the conversion of a mixture of 2-chloro-1,1,2,2-tetrafluoroethane (i.e., $\text{CHF}_2\text{CClF}_2$ or HCFC-124a) and 2-chloro-1,1,1,2-tetrafluoroethane (i.e., CF_3CHClF or HCFC-124) to a mixture comprising 2,2-dichloro-1,1,1-trifluoroethane (i.e., CHCl_2CF_3 or HCFC-123) and 1,1,1,2,2-pentafluoroethane (i.e., CF_3CHF_2 or HFC-125) in addition to unconverted starting materials. The mixture comprising HFC-125 and HCFC-123 may be obtained in the vapor phase by contacting a mixture of HCFC-124a and -124 over the catalysts of this invention optionally in the presence of a diluent selected from the group consisting of HF, HCl, nitrogen, helium, argon, and carbon dioxide. The disproportionation is preferably conducted at about 150°C to about 400°C, more preferably about 250°C to about 350°C. If used, the diluent gas, may be present in a molar ratio of diluent to haloethane of from about 1:1 to about 5:1. Of note are contact times of from about 10 seconds to about 60 seconds.

Dehydrofluorination

- 25 Included in this invention is a process for decreasing the fluorine content of a halogenated hydrocarbon compound by dehydrofluorinating said halogenated hydrocarbon compound in the presence of a catalyst composition comprising at least one chromium-containing component selected from the group consisting of the crystalline copper-substituted alpha-chromium oxide described above and said copper-substituted alpha-chromium oxide which has been treated with a fluorinating agent.

Halogenated hydrocarbon compounds suitable as starting materials for the dehydrofluorination process of this invention are typically saturated. Saturated halogenated hydrocarbon compounds suitable for the dehydrofluorination processes of this invention include those of the general formula $C_nH_aF_d$, wherein n is an integer from 2 to 6, a is an integer from 1 to 12, d is an integer from 1 to 13, and the sum of a and d is equal to $2n + 2$. The fluorine content of saturated compounds of the formula $C_nH_aF_d$ may be decreased in the presence of a catalyst composition comprising at least one chromium-containing component selected from the group consisting of the crystalline copper-substituted alpha-chromium oxide described above and said copper-substituted alpha-chromium oxide which has been treated with a fluorinating agent. This decrease in fluorine content is typically associated with removal of hydrogen fluoride (HF) from the molecule and is referred to herein as dehydrofluorination.

The dehydrofluorination reactions are typically conducted at temperatures of from about 200°C to about 500°C, preferably from about 300°C to about 450°C. The contact time in the reactor is typically from about 1 to about 360 seconds. Of note are contact times of from about 5 to about 120 seconds. Carrying out the dehydrofluorination reactions in the presence of an inert gas such as helium, argon, or nitrogen promotes the dissociation of the fluorinated carbon compound, but this practice can also lead to difficulties in separation and is not preferred.

The product of dehydrofluorination reaction consists of HF and the unsaturated fluorinated carbon compound resulting from loss of HF from the starting material. Specific examples of vapor phase dehydrofluorination reactions which may be carried out using the catalysts of this invention include the conversion of CH_3CHF_2 to $CH_2=CHF$, the conversion of CH_3CF_3 to $CH_2=CF_2$, the conversion of CF_3CH_2F to $CF_2=CHF$, the conversion of $CHF_2CH_2CF_3$ to $CHF=CHCF_3$, the conversion of $CHF_2CHF CF_3$ to $CHF=CF CF_3$, and the conversion of $CF_3CH_2CF_3$ to $CF_3CH=CF_2$.

Of note is a catalytic process for producing fluoroethene (i.e., $CH_2=CHF$ or vinyl fluoride) by the dehydrofluorination of a 1,1-difluoroethane (i.e., CHF_2CH_3 or HFC-152a). A mixture comprising vinyl fluoride and unconverted HFC-152a may be obtained in the vapor phase by contacting HFC-152a over the catalysts of this invention optionally in the presence of a diluent selected from the group consisting of HF,

nitrogen, helium, argon, and carbon dioxide. The dehydrofluorination is preferably conducted at about 150°C to about 400°C, more preferably about 250°C to about 350°C. If used, the diluent gas, may be present in a molar ratio of diluent to haloethane of from about 1:1 to about 5:1. Of note

5 are contact times of from about 10 seconds to about 60 seconds.

Chlorodefluorination

Included in this invention is a process for decreasing the fluorine content of a halogenated hydrocarbon compound by reacting said halogenated hydrocarbon compound with hydrogen chloride (HCl) in the vapor phase in the presence of a catalyst composition comprising at least one chromium-containing component selected from the group consisting of the crystalline copper-substituted alpha-chromium oxide described above and said copper-substituted alpha-chromium oxide which has been treated with a fluorinating agent.

15 Halogenated hydrocarbon compounds suitable as starting materials for the chlorodefluorination processes of this invention may be saturated or unsaturated. Saturated halogenated hydrocarbon compounds suitable for the chlorodefluorination processes of this invention include those of the general formula $C_nH_aCl_cF_d$, wherein n is an integer from 1 to 6, a is an integer from 0 to 12, c is an integer from 0 to 13, d is an integer from 1 to 13, and the sum of a, c and d is equal to $2n + 2$. Unsaturated halogenated hydrocarbon compounds suitable for the chlorodefluorination processes of this invention include those of the general formula $C_pH_eCl_gF_h$, wherein p is an integer from 2 to 6, e is an integer from 0 to 10, g is an integer from 0 to 12, h is an integer from 1 to 11, and the sum of e, g, and h is equal to $2p$. The fluorine content of saturated compounds of the formula $C_nH_aCl_cF_d$ and/or unsaturated compounds of the formula $C_pH_eCl_gF_h$ may be decreased by reacting said compounds with HCl in the vapor phase in the presence of a catalyst composition comprising at least one chromium-containing component selected from the group consisting of the crystalline copper-substituted alpha-chromium oxide described above and said copper-substituted alpha-chromium oxide which has been treated with a fluorinating agent. Such a process is referred to herein as a vapor phase chlorodefluorination reaction. Chlorodefluorination is disclosed in U.S. Patent No. 5,345,017 and U.S. Patent No. 5,763,698 and the teachings of these two patents are hereby incorporated herein by reference.

The chlorodefluorination reactions are typically conducted at temperatures of from about 250°C to 450°C, preferably from about 300°C

to about 400°C. The contact time in the reactor is typically from about 1 to about 120 seconds. Of note are contact times of from about 5 to about 60 seconds. The reactions are most conveniently carried out at atmospheric or superatmospheric pressure.

5 Chlorodefluorinations involving saturated halogenated hydrocarbons are of particular note. The molar ratio of HCl to the saturated halogenated hydrocarbon compound is typically from about 1:1 to about 100:1, preferably from about 3:1 to about 50:1, and most preferably from about 4:1 to about 30:1. In general, with a given catalyst
10 composition, the higher the temperature, the longer the contact time, and the greater the molar ratio of HCl to saturated halogenated hydrocarbon compound, the greater is the conversion to compounds having lower fluorine content. The above variables can be balanced, one against the other, so that the formation of chlorine- substituted products is maximized.

15 The product of chlorodefluorination reactions typically comprise unreacted HCl, HF, unconverted starting material, and saturated halogenated hydrocarbon compounds having a lower fluorine content than the starting material by virtue of the substitution of one or more fluorine substituents for chlorine. Specific examples of vapor phase
20 chlorodefluorination reactions which may be carried out using the catalysts of this invention include the conversion of CHF_3 to a mixture of CHCl_3 , CHCl_2F , and CHClF_2 , the conversion of $\text{CClF}_2\text{CClF}_2$ to a mixture of CCl_3CCl_3 , $\text{CCl}_3\text{CCl}_2\text{F}$, $\text{CCl}_3\text{CClF}_2$, $\text{CCl}_2\text{FCCl}_2\text{F}$, $\text{CClF}_2\text{CCl}_2\text{F}$, and CCl_3CF_3 , the conversion of CF_3CClF_2 to a mixture of CCl_3CCl_3 ,
25 $\text{CCl}_3\text{CCl}_2\text{F}$, $\text{CCl}_3\text{CClF}_2$, $\text{CCl}_2\text{FCCl}_2\text{F}$, $\text{CClF}_2\text{CCl}_2\text{F}$, CCl_3CF_3 , $\text{CClF}_2\text{CClF}_2$, and $\text{CF}_3\text{CCl}_2\text{F}$, the conversion of $\text{CF}_3\text{CCl}_2\text{CF}_3$ to a mixture of $\text{CF}_3\text{CCl}_2\text{CClF}_2$, $\text{CF}_3\text{CCl}_2\text{CCl}_2\text{F}$, $\text{CF}_3\text{CCl}_2\text{CCl}_3$, and $\text{CClF}_2\text{CCl}_2\text{CCl}_3$, and the conversion of $\text{CF}_3\text{CH}_2\text{CF}_3$ to a mixture of $\text{CCl}_2=\text{CHCF}_3$, and $\text{CCl}_2=\text{CClCF}_3$.

30 Of note is a catalytic process for producing a mixture containing 1,1-dichloro-3,3,3-trifluoro-1-propene (i.e., $\text{CCl}_2=\text{CHCF}_3$ or HCFC-1223za) and 1,1,2-trichloro-3,3,3-trifluoro-1-propene (i.e., $\text{CCl}_2=\text{CClCF}_3$ or CFC-1213xa) by the chlorodefluorination of 1,1,1,3,3,3-hexafluoropropane (i.e., $\text{CF}_3\text{CH}_2\text{CF}_3$ or HFC-236fa) by reaction of HFC-236fa with HCl in the
35 vapor phase in the presence of the catalysts of this invention. The reaction is preferably conducted from about 275°C to about 450°C, more preferably about 300°C to about 400°C with a molar ratio of HCl to HFC-236fa of preferably from about 3:1 to about 20:1. Of note are contacts

times of from about 1 second to about 40 seconds. Oxygen in the form of air or co-fed with an inert diluent such as nitrogen, helium, or argon may be added along with the reactants or as a separate catalyst treatment, if desired.

5 The reaction products obtained by the processes of this invention can be separated by conventional techniques, such as with combinations including, but not limited to, scrubbing, decantation, or distillation. Some of the products of the various embodiments of this invention may form one or more azeotropes with each other or with HF.

10 The processes of this invention can be carried out readily using well known chemical engineering practices.

Utility

Several of the reaction products obtained through use of the catalysts disclosed herein will have desired properties for direct commercial use. For example, CH_2F_2 (HFC-32), CHF_2CF_3 (HFC-125), CHF_2CH_3 (HFC-152a), CH_2FCF_3 (HFC-134a), $\text{CF}_3\text{CH}_2\text{CF}_3$ (HFC-236fa), and $\text{CF}_3\text{CH}_2\text{CHF}_2$ (HFC-245fa) find application as refrigerants, CH_2FCF_3 (HFC-134a) and CF_3CHF_2 (HFC-152a) find application as propellants, CH_3CHF_2 (HFC-152a) and $\text{CF}_3\text{CH}_2\text{CHF}_2$ (HFC-245fa) find application as blowing agents, and CHF_2CF_3 (HFC-125), $\text{CF}_3\text{CH}_2\text{CF}_3$ (HFC-236fa), and CF_3CHF_2 (HFC-227ea) find application as fire extinguishants.

Other reaction products obtained through the use of this invention are used as chemical intermediates to make useful products. For example, CCl_3CF_3 (CFC-113a) can be used to prepare CFC-114a which can then be converted to CH_2FCF_3 (HFC-134a) by hydrodechlorination. Similarly, $\text{CF}_3\text{CCl}_2\text{CF}_3$ (CFC-216aa) can be used to prepare $\text{CF}_3\text{CH}_2\text{CF}_3$ (HFC-236fa) by hydrodechlorination and $\text{CF}_3\text{CCl}=\text{CF}_2$ (CFC-1215zc) can be used to prepare $\text{CF}_3\text{CH}_2\text{CHF}_2$ (HFC-245fa) by hydrogenation.

Without further elaboration, it is believed that one skilled in the art can, using the description herein, utilize the present invention to its fullest extent. The following specific embodiments are, therefore, to be construed as merely illustrative, and do not constrain the remainder of the disclosure in any way whatsoever.

EXAMPLES

Catalyst Characterization

Energy Dispersive Spectroscopy (EDS) and Transmission Electron Microscopy (TEM)

5 In these studies, the crystallites were analyzed using a Philips CM-20 high-resolution transmission electron microscope operated at an accelerating voltage of 200 kV and configured with an Oxford windowless EDS system with a Si(Li) elemental detector. In the EDS analyses, electron-transparent thin sections of samples were used to minimize sample thickness effects such as fluorescence. Also, due to the similarity of their atomic masses, the X-ray absorption cross-sections for Cr and Cu were assumed to be the same (see the discussion by Zaluzec on pages 121 to 167 in *Introduction to Analytical Electron Microscopy* edited by J. J. Hren, J. I. Goldstein, and D. C. Joy (Plenum Press, New York, 1979). The samples were dispersed on Al grids to ensure that the Cu detected by the EDS analysis truly represented the Cu contained in the samples.

X-Ray Absorption Spectroscopy (XAS) and X-Ray Powder Diffraction (XRD)

20 XRD data were obtained and analyzed according to methods described by Warren in *X-Ray Diffraction* (Addison-Wesley, Reading, MA, 1969). XAS data were obtained at beamline 5BMD, DND-CAT, of the Advanced Photon Source, Argonne National Laboratory. XAS data were obtained and analyzed using the methods described in Koningsberger and Prins in *X-ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS and XANES* (John Wiley & Sons, New York, 1988). Spectra were obtained for the K edges of Cr, and Cu. Cr edges were obtained in transmission geometry, while Cu edges were obtained in fluorescence mode, due to their low concentrations.

30 Oxidation states were obtained by fitting of sample near edge spectra to those of standards with known oxidation states.

Use of the Advanced Photon Source for acquiring XAS data was supported by the U. S. Department of Energy, Office of Basic Energy Sciences, under Contract No. W-31-109-Eng-38.

Catalyst Preparations

COMPARATIVE PREPARATION EXAMPLE 1

Preparation of 100% Chromium Catalyst

A solution of 400 g $\text{Cr}(\text{NO}_3)_3[9(\text{H}_2\text{O})]$ (1.0 mole) in 1000 mL of deionized water was treated dropwise with 477 mL of 7.4M aqueous

ammonia raising the pH to about 8.5. The slurry was stirred at room temperature overnight. After re-adjusting the pH to 8.5 with ammonia, the mixture was poured into evaporating dishes and dried in air at 120°C. The dried solid was then calcined in air at 400°C; the resulting solid weighed 61.15 g. The catalyst was pelletized (-12 to +20 mesh, 1.68 to 0.84 mm) and 28.2 g (20 mL) was used in Comparative Example 1.

PREPARATION EXAMPLE 1

Preparation of 99% Chromium/1% Copper Catalyst

To a one liter beaker containing 261.0 g $\text{Cr}(\text{NO}_3)_3[9(\text{H}_2\text{O})]$ (0.652 mole) and 1.46 g $\text{Cu}(\text{NO}_3)_2[2.5 \text{H}_2\text{O}]$ (0.0063 mole) was added 100 mL of deionized water. The slurry was placed on a stirring hot plate in a fume-hood and heated while stirring until oxides of nitrogen started to evolve. The beaker containing the paste-like material was placed in a furnace in the fume-hood after removing the stirrer. The temperature of the furnace was raised to 150°C at the rate of 10 degrees/min and then to 550°C at the rate of 1 degree/minute. It was held at 550°C for an additional 10 hours. The resulting solid was pelletized (-12 to + 20 mesh, 1.68 to 0.84 mm) and 12.6 g (8.0 mL) was used in Examples 1 and 8.

PREPARATION EXAMPLE 2

Preparation of 99% Chromium/1% Copper Catalyst

In a 2000 mL beaker was placed 400.2 g $\text{Cr}(\text{NO}_3)_3[9(\text{H}_2\text{O})]$ (1.0 mole) and 1.64 g CuCl_2 (0.012 mole). To the solids was added 1000 mL deionized water. The mixture was stirred and when the dissolution was complete, the pH of the solution was raised from 2.0 to 8.0 by drop-wise addition of 8 molar aqueous ammonium hydroxide. The precipitated slurry was stirred for 24 hours at room temperature. It was then dried at 120-130°C overnight and calcined at 450°C for an additional 24 hours in air. The resulting solid was pelletized (-12 to + 20 mesh, 1.68 to 0.84 mm) and 11.0 g (8.0 mL) was used in Examples 2 and 9.

PREPARATION EXAMPLE 3

Preparation of 99% Chromium/1% Copper Catalyst

In a 3000 mL beaker was placed 500.0 g $\text{Cr}(\text{NO}_3)_3[9(\text{H}_2\text{O})]$ (1.25 moles) and 3.05 g $\text{Cu}(\text{NO}_3)_2[2.5 \text{H}_2\text{O}]$ (0.013 mole). To the solids was added 1200 mL deionized water. The mixture was stirred and when the dissolution was complete, the pH of the solution was raised from 2.4 to 8.5 by drop-wise addition of 300 mL of 8 molar aqueous ammonium hydroxide. The precipitated slurry was stirred for 24 hours at room temperature. It was then dried at 110-120°C overnight and calcined at

500°C for an additional 24 hours in air. The resulting solid was pelletized (-12 to +20 mesh, 1.68 to 0.84 mm) and 16.0 g (8.0 mL) was used in Examples 3 and 10.

PREPARATION EXAMPLE 4

5 Preparation of 98% Chromium/2% Copper Catalyst

Preparation Example 1 was substantially repeated except that the amount of chromium(III) nitrate was 258.0 g (0.645 mole) and the amount of copper (II) nitrate was 2.9 g (0.0125 mole). The resulting solid was pelletized (-12 to +20 mesh, 1.68 to 0.84 mm) and 12.6 g (8.0 mL) was used in Examples 4 and 11.

PREPARATION EXAMPLE 5

Preparation of 98% Chromium/2% Copper Catalyst

Preparation Example 2 was substantially repeated with 400.2 g chromium (III) nitrate (1.0 mole) and 3.31 g (0.0246 mole) copper (II) chloride. The solid, calcined in air at 450°C for 24 hours, was pelletized (-12 to +20 mesh, 1.68 to 0.84 mm) and 10.9 g (8.0 mL) was used in Examples 5 and 12.

PREPARATION EXAMPLE 6

Preparation of 98% Chromium/2% Copper Catalyst

20 In a 3000 mL beaker was placed 500.0 g $\text{Cr}(\text{NO}_3)_3[9(\text{H}_2\text{O})]$ (1.1.25 mole) and 6.1 g $\text{Cu}(\text{NO}_3)_2[2.5 \text{ H}_2\text{O}]$ (0.0262 mole). To the solids was added 1200 mL deionized water. The mixture was stirred and when the dissolution was complete, the pH of the solution was raised from 2.4 to 8.2 by drop-wise addition of 300 mL 8 molar aqueous ammonium hydroxide. 25 The precipitated slurry was stirred for 24 hours at room temperature. It was then dried at 110-120°C overnight and calcined at 500°C for an additional 24 hours in air. The resulting solid was pelletized (-12 to +20 mesh, 1.68 to 0.84 mm) and 14.9 g (8.0 mL) was used in Examples 6 and 13 as the catalyst.

PREPARATION EXAMPLE 7

Preparation of 95% Chromium/5% Copper Catalyst

Preparation Example 1 was substantially repeated except that the amount of chromium (III) nitrate was 250.0 g (0.625 mole) and the amount of copper (II) nitrate was 7.3 g (0.314 mole). The resulting solid was pelletized (-12 to +20 mesh, 1.68 to 0.84 mm) and 11.9 g (8.0 mL) was used in Examples 7 and 14.

PREPARATION EXAMPLES 8-9

Preparation of 95% Chromium/5% Copper Catalyst

Preparation Example 6 was substantially repeated except that the amounts of chromium (III) nitrate and copper (II) were adjusted to produce a catalyst having a ratio of chromium to copper of 95/5. The solid dried at 110-120°C overnight was divided into two portions. One portion was calcined at 500°C and another portion was calcined at 900°C. A 35.8 g (25.0 ml) portion, calcined at 500°C and pelletized to -12 to +20 mesh (1.68 to 0.84 mm), was used in Examples 8 and 15. Similarly a 48.1 g (25.0 ml) portion, calcined at 900°C and pelletized to -12 to +20 mesh (1.68 to 0.84 mm), was used in Examples 9 and 16.

EXAMPLES 1-7 and COMPARATIVE EXAMPLE 1

General Procedure for Fluorination and Chlorofluorination

A weighed quantity of pelletized catalyst was placed in a 5/8 inch (1.58 cm) diameter Inconel™ nickel alloy reactor tube heated in a fluidized sand bath. The tube was heated from 50°C to 175°C in a flow of nitrogen (50 cc/min; $8.3(10)^{-7} \text{m}^3/\text{sec}$) over the course of about one hour. HF was then admitted to the reactor at a flow rate of 50 cc/min ($8.3(10)^{-7} \text{m}^3/\text{sec}$). After 0.5 to 2 hours the nitrogen flow was decreased to 20 cc/min ($3.3(10)^{-7} \text{m}^3/\text{sec}$) and the HF flow increased to 80 cc/min ($1.3(10)^{-6} \text{m}^3/\text{sec}$); this flow was maintained for about 1 hour. The reactor temperature was then gradually increased to 400°C over 3 to 5 hours. At the end of this period, the HF flow was stopped and the reactor cooled to 300°C under 20 sccm ($3.3(10)^{-7} \text{m}^3/\text{sec}$) nitrogen flow. CFC-1213xa was fed from a pump to a vaporizer maintained at about 118°C. For fluorinations, the CFC-1213xa vapor was combined with the appropriate molar ratios of HF in a 0.5 inch (1.27 cm) diameter Monel™ nickel alloy tube packed with Monel™ turnings. The mixture of reactants then entered the reactor. The HF/1213xa molar ratio was 20 and the contact time was 5 seconds for Examples 1-7. For chlorofluorinations, the CFC-1213xa vapor was combined with the appropriate molar ratios of HF and chlorine. The HF/1213xa/chlorine molar ratio was 20/1/4 for all runs and the contact time was 5 seconds for Examples 8-14 and 30 seconds for Examples 15-16. The reactions were conducted at a nominal pressure of one atmosphere. Analytical data for identified compounds is given in units of GC area %. Small quantities of other unidentified products were present.

General Procedure for Fluorocarbon Product Analysis

The following general procedure is illustrative of the method used for analyzing the products of fluorination and chlorofluorination reactions. Part of the total reactor effluent was sampled on-line for organic product analysis using a gas chromatograph equipped a mass selective detector (GC-MS). The gas chromatography was accomplished with a 20 ft. (6.1 m) long x 1/8 in. (0.32 cm) diameter tubing containing Krytox® perfluorinated polyether on an inert carbon support. The helium flow was 30 mL/min ($5.0(10)^{-7}$ m³/sec). Gas chromatographic conditions were 60°C for an initial hold period of three minutes followed by temperature programming to 200°C at a rate of 6°C/minute.

The bulk of the reactor effluent containing organic products and also inorganic acids such as HCl and HF was treated with aqueous caustic prior to disposal.

15 Legend

214ab is $\text{CF}_3\text{CCl}_2\text{CCl}_2\text{F}$	215aa is $\text{CF}_3\text{CCl}_2\text{CClF}_2$
215bb is $\text{CCl}_2\text{FCClFCF}_3$	216aa is $\text{CF}_3\text{CCl}_2\text{CF}_3$
216ca is $\text{CClF}_2\text{CF}_2\text{CClF}_2$	216cb is $\text{CF}_3\text{CF}_2\text{CCl}_2\text{F}$
216ba is $\text{CClF}_2\text{CClFCF}_3$	217ba is $\text{CF}_3\text{CClFCF}_3$
20 217ca is $\text{CF}_3\text{CF}_2\text{CClF}_2$	225da is $\text{CF}_3\text{CHClCClF}_2$
226da is $\text{CF}_3\text{CHClCF}_3$	1213xa is $\text{CF}_3\text{CCl}=\text{CCl}_2$
1214 is $\text{C}_3\text{Cl}_2\text{F}_4$	1215xc is $\text{CF}_3\text{CCl}=\text{CF}_2$

EXAMPLES 1-7

FLUORINATION OF 1213xa

25 The fluorination of CFC-1213xa was carried out at various temperatures using catalysts prepared according to Catalyst Preparation Examples 1-7. The analytical results are shown in Table 1.

TABLE 1

Ex..	Cat	T°C	1215xc	226da	216aa	1214	225da	215aa	215bb	1213xa
30	No.	Prep.								
	1	1	280	17.9	64.8	5.0	4.0	3.5	1.2	2.8
			320	8.3	85.0	3.1	1.8	0.6	0.2	0.8
	2	2	280	3.1	90.9	3.2	0.5	0.9	0.6	0.4
35			300	1.3	93.5	3.8	0.2	0.2	0.4	0.2
			320	1.7	93.7	3.3	0.3	0.2	0.2	0.2

TABLE 1 (continued)

	Ex. No.	Cat Prep.	T°C	1215xc	226da	216aa	1214	225da	215aa	215bb	1213xa
5	3	3	280	25.0	57.1	4.5	4.9	5.2	1.1	ND	2.1
			320	8.5	83.3	4.4	2.1	0.6	0.3	ND	0.8
10	4	4	280	53.3	7.3	2.7	11.5	3.6	2.5	1.2	17.7
			320	62.2	12.3	2.5	13.3	2.7	0.9	ND	6.0
	5	5	280	53.7	12.8	2.4	12.0	5.5	1.9	ND	11.1
			320	59.4	14.2	1.7	13.9	3.8	0.1	ND	6.3
			350	56.7	21.7	3.5	11.0	1.8	ND	ND	3.4
	6	6	280	51.8	23.6	3.9	7.8	3.9	1.5	ND	7.2
320			49.0	29.0	4.0	10.3	2.4	0.4	ND	4.8	
20	7	7	280	28.9	0.6	1.0	16.0	0.2	1.5	1.5	50.3
			320	51.3	0.8	2.2	19.6	0.6	2.4	0.3	22.7
			350	68.5	0.9	2.8	16.3	ND	0.7	ND	9.6
	Comp. Ex. 1		300	ND	89.7	7.8	ND	ND	ND	ND	ND
	ND = not detected										

ND = not detected

Examination of the data in the fluorination examples above show that the fluorine content of the starting CFC-1213xa is increased to produce CFC-1215xc, HCFC-226da as well as other useful products containing a higher fluorine content than the starting material by using the catalysts of this invention.

EXAMPLES 8-16

30 CHLOROFLUORINATION OF 1213xa

The chlorofluorination of CFC-1213xa was carried out at various temperatures using catalysts prepared according to Catalyst Preparation Examples 1-9. The analytical results are shown in Table 2.

TABLE 2

	Ex..	Cat	T°C	217ba	217ca	1215xc	226da	216aa	216ba	216cb	215aa	215bb	214ab	1214
	No.	Prep.												
5	8	1	280	0.7	ND	0.9	2.4	14.4	4.8	0.6	63.4	8.5	3.2	0.3
			320	3.4	0.3	1.0	2.4	36.3	14.8	1.2	38.9	1.4	ND	ND
			375	5.8	1.3	0.3	1.4	60.2	13.7	0.4	16.7	ND	ND	ND
10	9	2	280	0.4	ND	0.4	1.4	13.2	7.6	0.8	61.0	13.8	ND	ND
			320	1.4	0.4	0.2	1.4	31.1	23.3	1.0	41.1	0.1	ND	ND
			375	3.2	1.2	0.1	0.8	59.3	16.7	0.2	18.4	0.1	ND	ND
15	10	3	320	2.4	0.4	0.3	0.8	32.8	26.6	2.0	33.5	1.1	ND	ND
			350	2.9	1.1	0.3	0.5	42.3	26.5	1.4	24.8	ND	ND	ND
			375	3.4	1.6	0.1	0.5	53.6	21.8	0.5	18.5	ND	ND	ND
20	11	4	280	0.2	ND	1.7	0.4	11.0	2.3	1.4	26.5	33.6	18.2	4.7
			320	0.4	ND	0.9	0.5	21.0	12.1	1.9	41.8	20.4	0.8	0.1
			350	0.5	0.2	0.6	0.4	28.1	21.2	2.5	36.8	9.4	0.1	ND
25	12	5	350	0.2	0.2	0.2	0.2	18.4	28.8	1.7	45.5	4.7	ND	ND
			375	0.3	0.5	0.2	0.1	24.4	30.6	1.6	41.4	0.7	ND	ND
			400	0.6	0.9	0.2	0.1	31.5	28.5	1.2	36.7	0.2	ND	ND
30	13	6	320	0.3	0.2	0.2	0.2	16.3	27.7	2.4	41.7	10.3	ND	ND
			350	0.9	0.8	0.3	0.2	26.7	33.1	2.0	33.9	2.0	ND	ND
			375	2.2	1.8	0.1	0.1	44.3	28.4	0.8	21.8	0.4	ND	ND
35	14	7	320	ND	ND	1.1	0.1	8.5	4.3	1.5	39.6	36.0	7.8	1.0
			350	0.1	0.1	0.9	0.1	10.9	10.4	2.0	42.9	30.9	1.6	0.3
			400	0.1	0.1	0.6	ND	12.4	19.8	1.9	46.8	17.9	0.3	0.1
35	15	8	280	ND	ND	0.8	ND	3.5	0.9	0.5	26.7	36.0	26.5	4.6
			320	ND	ND	1.9	ND	6.7	11.8	0.8	49.8	27.2	0.7	0.3
			425	ND	ND	0.9	0.2	5.5	25.7	0.7	59.1	5.9	0.1	0.2
35	16	9	280	ND	ND	0.3	ND	2.9	0.4	0.6	20.2	47.3	25.9	1.9
			320	ND	ND	0.3	ND	3.8	1.4	1.0	29.3	48.4	14.3	1.1
			425	ND	ND	0.3	ND	5.1	12.8	1.4	50.8	28.1	0.6	0.2

TABLE 2 (continued)

5 Examination of the data in the chlorofluorination examples above
show that the fluorine content of the starting CFC-1213xa is increased to
produce CFC-216aa and CFC-216ba as well as other useful products
containing a higher fluorine content than the starting material by using the
catalysts of this invention.

10 The examples above illustrate use of the catalysts of this invention
to increase the fluorine content of a compound. Using the catalysts of this
invention, the fluorine distribution in a halogenated hydrocarbon
compound may be changed by isomerization or disproportionation or the
fluorine content of a compound may be decreased by dehydrofluorination
or by reaction with hydrogen chloride in a manner analogous to the
15 teachings of International Publication No. WO 2004/018093 A2, which is
incorporated herein by reference.

CLAIMS

What is claimed is:

- 5 1. A crystalline alpha-chromium oxide where from about 0.05 atom % to about 5 atom % of the chromium atoms in the alpha-chromium oxide lattice are replaced by divalent copper atoms.
- 10 2. A chromium-containing catalyst composition comprising as a chromium-containing component the crystalline copper-substituted alpha-chromium oxide of Claim 1.
- 15 3. A chromium-containing catalyst composition comprising a chromium-containing component prepared by treating the crystalline copper-substituted alpha-chromium oxide of Claim 1 with a fluorinating agent.
- 20 4. A process for changing the fluorine distribution in a hydrocarbon or a halogenated hydrocarbon in the presence of a catalyst, characterized by:
 using as the catalyst a composition comprising at least one chromium-containing component selected from the group consisting of the crystalline copper-substituted alpha-chromium oxide of Claim 1 and a crystalline copper-substituted alpha-chromium oxide of Claim 1 which has been treated with a fluorinating agent.
- 25 5. The process of Claim 4 wherein the fluorine content of a halogenated hydrocarbon compound or an unsaturated hydrocarbon compound is increased by reacting said compound with hydrogen fluoride in the vapor phase in the presence of said catalyst composition.
- 30 6. The process of Claim 4 wherein the fluorine content of a halogenated hydrocarbon compound or a hydrocarbon compound is increased by reacting said compound with HF and Cl₂ in the vapor phase in the presence of said catalyst composition.
- 35 7. The process of Claim 4 wherein the fluorine distribution in a halogenated hydrocarbon compound is changed by isomerizing said

halogenated hydrocarbon compound in the presence of said catalyst composition.

8. The process of Claim 4 wherein the fluorine distribution in a halogenated hydrocarbon compound is changed by disproportionating said halogenated hydrocarbon compound in the vapor phase in the presence of said catalyst composition.

9. The process of Claim 4 wherein the fluorine content of a halogenated hydrocarbon compound is decreased by dehydrofluorinating said halogenated hydrocarbon compound in the presence of said catalyst composition.

10. The process of Claim 4 wherein the fluorine content of a halogenated hydrocarbon compound is decreased by reacting said halogenated hydrocarbon compound with hydrogen chloride in the vapor phase in the presence of said catalyst composition.

11. A method for preparing a composition comprising the crystalline copper-substituted alpha-chromium oxide of Claim 1, comprising:

(a) co-precipitating a solid by adding ammonium hydroxide to an aqueous solution of a soluble copper salt and a soluble trivalent chromium salt that contains at least three moles of nitrate per mole of chromium in the solution and has a copper concentration of from about 0.05 atom % to about 5 atom % of the total concentration of copper and chromium in the solution; and after at least three moles of ammonium per mole of chromium in the solution has been added to the solution;

(b) collecting co-precipitated solid formed in (a);

(c) drying the collected solid; and

(d) calcining the dried solid.

12. The method of Claim 11 wherein the soluble copper salt is a divalent copper salt.

13. The method of Claim 12 wherein the soluble copper and chromium salts are nitrates or hydrated nitrates

14. The method of Claim 12 wherein more than three moles of ammonium nitrate per mole of chromium is present in the aqueous solution.

- 5 15. A method for preparing a composition comprising the crystalline copper-substituted alpha-chromium oxide of Claim 1, comprising:
- (a) preparing an aqueous solution of a soluble copper salt and a soluble trivalent chromium salt that contains a copper concentration of from about 0.05 atom % to about 5 atom % of the total concentration of
- 10 copper and chromium in the solution;
- (b) evaporating the solution to dryness; and
- (c) calcining the dried solid.

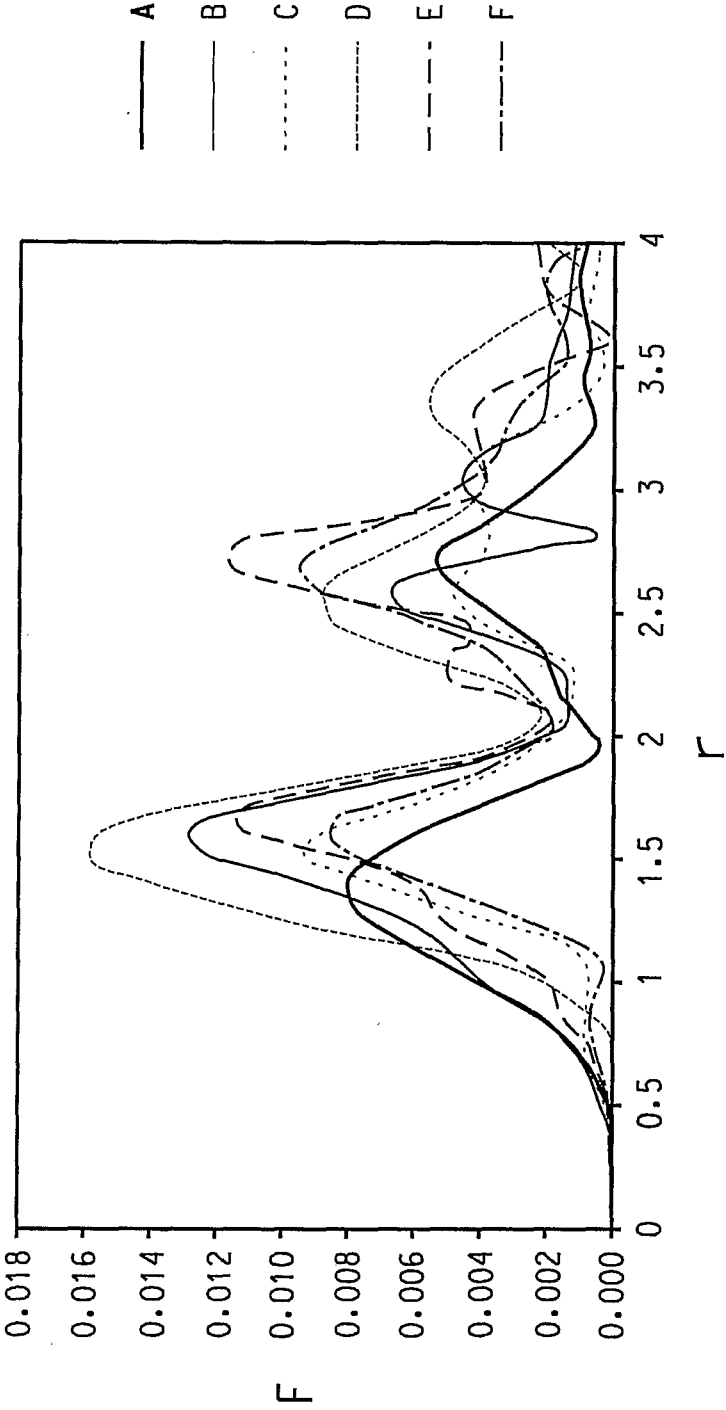


FIG. 1