ABSTRACT

Described are a process and method to synthesize ultrafine materials such as metal oxides and highly dispersed mixed metal oxides. A process for forming an ultrafine material comprises mixing two or more liquid precursor compositions in a mixing apparatus to form a precursor mixture, wherein the mixing apparatus is in fluid communication with an atomizer; atomizing the precursor mixture in the atomizer to form droplets; directing the droplets to a reaction chamber in communication with a volumetric heating source; wherein the a reaction chamber is in fluid communication with the atomizer; volumetrically heating the droplets to produce the ultrafine material; and isolating the ultrafine material.
FIG. 4

CPS

0 10000 20000 30000 40000

20 40 60 80 100 (Deg.)

Cat 2 (ground)
Cat 2 (unground)
Cat 1 (ground)
Cat 1 (unground)

Phase B (3122)

FIG. 5

FIG. 6
A process for forming an ultrafine material comprises mixing two or more liquid precursor compositions in a mixing apparatus to form a precursor mixture, wherein the mixing apparatus is in fluid communication with an atomizer; atomizing the precursor mixture in the atomizer to form droplets; directing the droplets to a reaction chamber in communication with a volumetric heating source, wherein the reaction chamber is in fluid communication with the atomizer; volumetrically heating the droplets to produce the ultrafine material; and isolating the ultrafine material.

A second process for forming an ultrafine material comprises atomizing a first liquid precursor in an atomizer to form droplets; directing the droplets to a reaction chamber in communication with a volumetric heating source, wherein the reaction chamber is in fluid communication with the atomizer, and wherein the reaction chamber comprises a second liquid precursor; volumetrically heating the first and second precursors to produce the ultrafine material; and isolating the ultrafine material.

Yet another process for forming an ultrafine material comprises atomizing a first liquid precursor in a first atomizer to form first precursor droplets while simultaneously atomizing a second liquid precursor in a second atomizer to form second precursor droplets, wherein the first atomizer and the second atomizer are in fluid communication with a reaction chamber; directing the first precursor droplets and the second precursor droplets to the reaction chamber, wherein the reaction chamber is in communication with a volumetric heating source; volumetrically heating the first precursor droplets and the second precursor droplets to produce the ultrafine material, and isolating the ultrafine material.

An alternative apparatus for forming an ultrafine material comprises a first atomizer and a second atomizer in fluid communication with a reaction chamber, and a volumetric heating source to irradiate droplets formed by the atomizer; wherein the volumetric heating source is in communication with the reaction chamber.

brief description of the drawings

Fig. 1 shows an embodiment of an apparatus suitable for performing the INM process. Fig. 2 shows an embodiment of an apparatus for a nozzle-microwave process. Fig. 3 shows a schematic of a bulk microwave reactor. Fig. 4 shows x-ray diffraction data for a catalyst made by a control bulk method compared to a catalyst prepared by the disclosed INM method. Fig. 5 shows an SEM analysis of control example 1 Catalyst 1. Fig. 6 shows an SEM analysis of inventive example 1 Catalyst 2.

A process for forming an ultrafine material comprises mixing two or more liquid precursor compositions in a mixing apparatus to form a precursor mixture, wherein the mixing apparatus is in fluid communication with an atomizer; atomizing the precursor mixture in the atomizer to form droplets; directing the droplets to a reaction chamber in communication with a volumetric heating source, wherein the reaction chamber is in fluid communication with the atomizer; volumetrically heating the droplets to produce the ultrafine material; and isolating the ultrafine material.

Another process for forming an ultrafine material comprises atomizing a first liquid precursor in an atomizer to form droplets; directing the droplets to a reaction chamber in communication with a volumetric heating source, wherein the reaction chamber is in fluid communication with the atomizer, and wherein the reaction chamber comprises a second liquid precursor; volumetrically heating the first and second precursors to produce the ultrafine material; and isolating the ultrafine material.

Yet another process for forming an ultrafine material comprises atomizing a first liquid precursor in a first atomizer to form first precursor droplets while simultaneously atomizing a second liquid precursor in a second atomizer to form second precursor droplets, wherein the first atomizer and the second atomizer are in fluid communication with a reaction chamber; directing the first precursor droplets and the second precursor droplets to the reaction chamber, wherein the reaction chamber is in communication with a volumetric heating source; volumetrically heating the first precursor droplets and the second precursor droplets to produce the ultrafine material, and isolating the ultrafine material.

An alternative apparatus for forming an ultrafine material comprises a first atomizer and a second atomizer in fluid communication with a reaction chamber, and a volumetric heating source to irradiate droplets formed by the atomizer; wherein the volumetric heating source is in communication with the reaction chamber.

FIG. 1 shows an embodiment of an apparatus suitable for performing the INM process. FIG. 2 shows an embodiment of an apparatus for a nozzle-microwave process. FIG. 3 shows a schematic of a bulk microwave reactor. FIG. 4 shows x-ray diffraction data for a catalyst made by a control bulk method compared to a catalyst prepared by the disclosed INM method. FIG. 5 shows an SEM analysis of control example 1 Catalyst 1. FIG. 6 shows an SEM analysis of inventive example 1 Catalyst 2.
FIG. 7 shows X-ray diffraction (XRD) patterns of zeolite-A prepared with: no microwave, no nozzle, 1 sccm flow rate (A); no microwave, 48 kHz nozzle, 1 sccm flow rate (B); or 100 W microwave, no nozzle, 1 sccm flow rate (C).

FIG. 8 shows FESEM micrographs of zeolite-A prepared with no microwave, no nozzle, 1 sccm flow rate (A); no microwave, 48 kHz nozzle, 1 sccm flow rate (B); or 100 W microwave, no nozzle, 1 sccm flow rate (C).

FIG. 9 shows XRD patterns of zeolite-A prepared with microwave and nozzle: 100 W microwave, 48 kHz nozzle, 0.4 sccm flow rate, not seeded (A); 100 W microwave, 48 kHz nozzle, 0.4 sccm flow rate, seeded (B); and 200 W microwave, 48 kHz nozzle, 0.4 sccm flow rate, seeded (C).

FIG. 10 shows FESEM micrographs of zeolite-A prepared with microwave and nozzle: 100 W microwave, 48 kHz nozzle, 0.4 sccm flow rate, not seeded (A); 100 W microwave, 48 kHz nozzle, 0.4 sccm flow rate, seeded (B); and 200 W microwave, 48 kHz nozzle, 0.4 sccm flow rate, seeded (C).

FIG. 11 shows XRD patterns of zeolite-A prepared with microwave and nozzle at varying microwave power: 50 W microwaves, 48 kHz nozzle, 0.4 sccm flow rate (A); 100 W microwaves, 48 kHz nozzle, 0.4 sccm flow rate (B); and 200 W microwaves, 120 kHz nozzle, 0.4 sccm flow rate (C).

FIG. 12 shows XRD patterns of zeolite-A prepared with microwave and nozzle at varying precursor flow rates, aging and microwave power using TMA*: 100 W microwaves, 48 kHz nozzle, 0.4 sccm flow rate, precursors aged for 0 days (A); 100 W microwaves, 48 kHz nozzle, 1.0 sccm flow rate, precursors aged for 1 day (B); 100 W microwaves, 48 kHz nozzle, 0.4 sccm flow rate, precursors aged for 1 day (C); 200 W microwaves, 48 kHz nozzle, 1.0 sccm flow rate, precursors aged for 1 day (D); and 200 W microwaves, 48 kHz nozzle, 2.0 sccm flow rate, precursors aged for 0 days (E).

FIG. 13 shows FESEM micrographs of zeolite-A prepared with conventional microwave at 80° C. for 30 minutes.

FIG. 14 shows XRD patterns of nickel ferrite synthesized from different conditions using carbonate as the co-precipitant: no microwaves, no nozzle (A); no microwaves, 120 kHz nozzle, 1 sccm flow rate (B); 100 W microwaves, 48 kHz nozzle, 1 sccm flow rate (C); 100 W microwaves, 120 kHz nozzle, 1 sccm flow rate (D); 300 W microwaves, 0 kHz nozzle (i.e., no nozzle), 1 sccm flow rate (E); 300 W microwaves, 120 kHz nozzle, 1 sccm flow rate (F); and 300 W microwaves, 120 kHz nozzle, 3 sccm flow rate (G). When the ultrasonic nozzle and appropriate microwave power and precursor flow rates are utilized, purer nickel ferrite with small crystallite size are obtained. In each case calculations were done at 800° C. for 3 hours.

FIG. 15 shows XRD patterns of nickel ferrite synthesized from different conditions using hydroxide as the co-precipitant: no microwaves, no nozzle, 1 sccm flow rate (A); 100 W microwave, no nozzle, 1 sccm flow rate (B); 0 W microwave, 120 kHz nozzle, 1 sccm flow rate (C); 300 W microwave, no nozzle (D); 300 W microwave, 120 kHz nozzle, 1 sccm flow rate, only co-precipitant (NaOH) sprayed (E); 300 W microwave, 120 kHz nozzle, 1 sccm flow rate (F); and 400 W microwave, 120 kHz nozzle, 1 sccm flow rate (G). When the ultrasonic nozzle and appropriate microwave power and precursor flow rates are utilized, purer nickel ferrite with small crystallite size are obtained.

The same observation as earlier noted for the synthesis of zeolite-A that microwave radiation and ultrasonic spray nozzle do compliment each other. The effects of microwave power, flow rates or nozzle usage are consistent when different co-precipitants are used. When both nozzle and minimum microwave power was used and a slow precursor flow rate, purer nickel ferrite with small crystallite size was obtained. FIGS. 14-15. Runs with no nozzle but with microwaves resulted in impurities comprising of nickel oxide hydroxide, goethite and ferricyanide. The impurity peaks are more prevalent particularly when no nozzle is used. FT-IR spectra (not included) of the optimized run showed the expected absorption bands of pure nickel ferrite.

Continuous synthesis using both the microwave radiation and ultrasonic nozzle resulted in average crystallite sizes as low as 4 nm as determined from X-ray diffraction data using Debye-Scherrer formula.

The above-described and other features will be appreciated and understood by those skilled in the art from the following detailed description, drawings, and appended claims.

DETAILED DESCRIPTION

One novel process to synthesize ultrafine materials comprises mixing two or more liquid precursor compositions in a mixing apparatus to form a precursor mixture, wherein the mixing apparatus is in fluidic communication with an atomizer, atomizing the precursor mixture in the atomizer to form droplets; directing the droplets to a reaction chamber in communication with a volumetric heating source, wherein the reaction chamber is in fluidic communication with the atomizer, volumetrically heating the droplets to produce the ultrafine material; and isolating the ultrafine material. The mixing process can be referred to as an in-situ mixing process. By in situ mixing, it is meant that the liquid precursor compositions are mixed in a mixing apparatus that is in fluidic communication with the atomizer. This is in contrast to a bulk process in which precursors are mixed, added to the reaction chamber in bulk, and reacted in the reaction chamber in bulk. The in situ mixing, atomizing and reacting can be done as a continuous process in contrast to a bulk process. One example of a volumetric heating source is a microwave source. The overall process can be referred to as INM for In situ, Nozzle and Microwave.

Also included is an apparatus for the INM process comprising three components in operable communication, the first component is a mixing apparatus, which is employed to inject substantially simultaneously two precursor solutions (A and B) connected, for example, by a T-connector. The second component is an atomizer, such as an ultrasonic nozzle spray, which is employed to form droplets (e.g., spray effect) when a liquid is injected through the feed tube of the nozzle. The third component is a reaction chamber in communication with a volumetric heating source, which is used to irradiate the droplets formed by the nozzle as they pass through the chamber. The mixing
apparatus and the atomizer are in fluid communication, and the atomizer and the reaction chamber are in fluid communication. The novel combination of these three components in one process is useful for making ultrafine materials such as, for example, metal oxides and highly dispersed mixed metal oxides.

[0032] The INM process includes in situ mixing of two of more liquid precursor compositions in a mixing apparatus to form a mixture. The mixing apparatus may include a syringe pump to inject simultaneously the two or more solutions to be mixed through, for example, a T-connector. The mixture of the precursor solutions may form a precipitate upon mixing, resulting in reproducible controlled steps of nucleation. The mixing apparatus may comprise a micronizer. In a micronizer, two or more liquids from their respective supply chambers are divided into spatially separate fluid streams using a network of microchannels allocated to the respective streams. The streams then merge as jets with substantially identical volumetric flow for each fluid into a mixing or reaction chamber in which they are mixed by diffusion and/or turbulence. In one embodiment, substantially identical volumetric flows of each fluid are introduced into the mixing or reaction chamber through the microchannels so that the mixing ratios do not substantially vary spatially within the mixing or reaction chamber. Variation in the mixing ratios may distort the mixing or reaction result.

[0033] In the INM process, after the liquid precursors are mixed, the mixture is atomized with an atomizer to form droplets. Atomization may be performed in the presence of a carrier gas such as an inert gas to assist in the formation of droplets. Atomization can be performed using a suitable atomization device, for example, a spray nozzle atomizer such as a pressure nozzle device, a two-fluid nozzle device; a rotary atomization device; a sonic energy atomizer that uses energy from a gas stream; an ultrasonic atomizer that uses electronic energy; atomizers that use electrostatic energy, an aspirator and an atomizer, and the like. An ultrasonic nozzle, for example, may be employed to produce vibrations, which cause the liquid coming from the in situ mixing of the liquid precursors to shear into small drops (e.g., spray or aerosol effect). When an ultrasonic nozzle is employed, the sonic power may be about 0.01 to about 3,000 watts.

[0034] At least three parameters may be adjusted to ensure that the liquid precursors do not significantly plug the nozzle: (1) when the precursor liquids are mixed in situ, substantially no solids should be formed that are of a size that could block the inner tube of the atomizer, (2) the speed at which the precursor liquids are injected into the nozzle can be adjusted so that it does not exceed the speed at which the material comes out of the nozzle, and (3) the viscosity of the mixed solution should be appropriate for the diameter of the nozzle.

[0035] In an alternative embodiment, in situ mixing and atomization are combined by using two atomizers, one containing solution A and one containing solution B. The two atomizers are placed in fluid communication with a reaction chamber in communication with a volumetric heating source. In one embodiment, two atomizers are placed so that they direct the droplets towards the reaction chamber where they react. An alternative embodiment of an apparatus thus includes a first atomizer and a second atomizer in fluid communication with a reaction chamber; and a reaction chamber in communication with a volumetric heating source to irradiate droplets formed by the atomizer.

[0036] After the precursors are atomized, they are volumetrically heated in the reaction chamber to convert them to the final ultrafine material. In many conventional radiative heating methods, thermal energy is absorbed on the surface and then is transferred towards the interior of the droplets via thermal conductivity. There is an energy transfer (i.e., not conversion) in these methods, and the process is slow. In non-radiative methods such as, for example, microwave heating, the microwaves are absorbed by the material as a whole, due to deep penetration, and then converted to heat via either dielectric loss mechanisms and/or eddy current losses in electrically conducting materials. Heating that occurs through dielectric loss, for example, occurs from the inside to the outside of the object to be heated. Heating processes that involve energy conversion are collectively known as volumetric heating processes. While radiative and volumetric processes both result in thermal differentials, the thermal differentials are opposite. That is, radiative heating occurs from the outside to the inside, while volumetric heating occurs from the inside to the outside. Since there is an energy conversion in volumetric heating, the heating is very rapid.

[0037] In addition to microwaves, plasmas, radiofrequency waves, are discharges, and laser irradiation can be employed to volumetrically heat a sample. In the case of a plasma or arc discharge, there are excited state species that are at high electronic energies that can produce chemical reactions. The electrical energy of the plasma is converted to thermal energy to produce chemical reactions.

[0038] Suitable energy sources for volumetric heating include, for example, a pulsed or continuous wave laser source, a flashlamp or filament lamp, a radiofrequency source, a microwave source, an ac discharge source, a dc discharge source, and a corona discharge source.

[0039] Volumetric heating is employed to decrease reaction times and increase precursor dispersion. As shown herein, volumetric heating sources such as microwaves produce much more highly dispersed metal atom clusters than was possible by other methods. Use of a volumetric heating source can result in the production of materials of smaller particle size and greater particle size uniformity than other methods. The continuous volumetric heating process permits production of powders at much higher rates than other processes.

[0040] In a continuous volumetric heating process, the conversion of precursors to form the ultrafine material occurs while the reaction mixture is flowing through the reactor. In a batch volumetric heating process, the energy is applied to the reaction mixture by means such as a microwave oven. The batch procedure generally does not allow the energy to be localized to the vicinity of the reaction. In the case of a millimeter-wave beam driven batch process, the energy can be localized to the vicinity of the reaction.

[0041] A microwave process can be performed with different types of microwave systems, all of which can effectively localize the microwave power in the reactor. A microwave system comprises a reaction chamber in communication with a microwave source. One type of
microwave system is a single pass, traveling wave applicator, where microwave energy propagates down the length of a waveguide, where the maximum field and power is concentrated at the center of the waveguide where the reaction tube is located. A second type of microwave system is a standing wave system where the microwaves are introduced into a tuned chamber, which concentrates the microwave energy at the location of the reaction tube. A third microwave system is a beam system, where microwave energy is focused onto the reactor through which the precursor liquids flow. Suitable sources of microwaves or energy include, but are not limited to, a magnetron and a gyrotron. Suitable frequencies include, but are not limited to about 2.45 GHz to about 7 GHz. Suitable microwave powers are up to, but not limited to 1300 watts. The time of microwaving will depend upon several factors including the microwave energy and frequency, the reactants and kinetics of the reaction to be performed.

[0042] In one embodiment, a microwave source is employed to induce a plasma. A plasma is produced by the breakdown of gas to form electrons and ions through an electric field, wherein the electrons are accelerated by an electromagnetic field such as microwaves and collide with the gas to induce production of ions and electrons, such that electrons and ions are continuously generated until equilibrium of such production and depletion is reached to thereby form a stable plasma. Besides ions and electrons, the plasma also contains highly reactive species of an excited or transient state and free radicals, which can be used to perform reactions that are difficult to implement. A microwave plasma can be formed in a static chamber or in a flow system such as a plasma jet reactor. The microwave plasma device can include a shroud that produces a plasma over a large volume. The materials produced using a microwave plasma may have different properties than those produced by simple microwave heating.

[0043] After the precursors react and the ultrafine material is produced, the reaction mixture may be further treated with, for example, conventional radiative heating methods using, for example, heat or light. Such treatment may produce different properties in the material produced than volumetric heating alone.

[0044] After the precursors react and the ultrafine material is produced, the reaction mixture may be cooled either naturally (e.g., air-cooling) or quenched (e.g., forced cooling). Quenching can provide greater control over the reaction time than air-cooling. Once the product has achieved room temperature, the product may be subjected to filtering, rinsing, drying, and/or calcining procedures depending upon the material prepared. Calcining may be employed to achieve the desired crystalline phases in the material that is produced. Heating sources for calcining include microwave sources and conventional thermal heating sources. The post-treatment may be performed in different environments such as, for example, air, N₂, O₂, or H₂.

[0045] In an alternative process to form ultrafine materials, referred to as NM for nozzle-microwave, an atomizer in fluid communication with a reaction chamber is employed to direct droplets of a first liquid precursor to the reaction chamber comprising the second liquid precursor. In this embodiment, a second liquid precursor is volumetrically heated in the reaction chamber while the first liquid precursor is added. The reaction chamber is in communication with a volumetric heating source. The precursors are volumetrically heated to produce the ultrafine material and the ultrafine material is isolated.

[0046] Variables of the INM and NM processes include: sonication power, droplet size, volumetric heating source, heating source power, heating source frequency, and heating source irradiation time. The proposed INM and NM processes are limited to the use of liquid precursors with appropriate viscosities but it is not limited to the type of material to be prepared.

[0047] The materials produced by the INM and NM processes can have maximum diameters from nanometers to about 100 micrometers, for example.

[0048] Both the INM and NM process employ liquid precursor compositions. Liquid precursor compositions comprise at least one precursor molecule suitable for the production of the ultrafine material and include, for example, liquid solutions, neat liquids and dispersions. Liquid solutions and dispersions can include a suitable solvent. Suitable solvents include water, inorganic solvents, alcohols, hydrocarbons, otherorganic solvents, and combinations comprising one or more of the foregoing solvents.

[0049] The precursor form for a metal will depend upon the metal itself. The precursor molecule may comprise at least one metal component comprising aluminum, boron, tin, thallium, antimony, lithium, sodium, potassium, strontium, yttrium, zirconium, barium, titanium, lead, samarium, rubidium, lanthanum, indium, nickel, copper, cobalt, calcium, magnesium, manganese, bismuth, zinc, silicon, germanium, nickel, tantalum, vanadium, iron, chromium, cadmium, molybdenum, antimony, cesium, gallium, niobium, silver, selenium, tungsten, tellurium, thorium, palladium, arsenic, platinum, rhodium, ruthenium, uranium, gold, silver, and combinations comprising one or more of the foregoing metal components.

[0050] The precursor (e.g., metal precursor) may be in elemental form, salt form, or in the form of an organometallic compound. When in the form of a salt, the salt comprises a metal cation and an anion. Suitable anions for the metal salts include, for example, hydroxides; phosphates; halides, such as fluoride, chloride, bromide, and iodide; oxalates; citrates; hydroxides; chalcogenides such as sulfide, selenide, and telluride; oxides; nitrates; nitrites; sulfites; sulfates; acetates; and carbonates; oxalate, acetacetonate, ammonia, amine, silicate, oxometalate, and combinations comprising one or more of the foregoing anions. Organometallic compounds are metal-organic radicals including the foregoing metals and an organic radical component comprising alkyl, aryloxy, aminoalkoxy, acetox, acetooctoynyl and combinations comprising one or more of the foregoing additives.

[0051] The liquid precursor composition may also comprise additives such as, for example, glucose, nitric acid, naphtha, toluene, benzene, hexane, nitric acid, acetic acid, oxalic acid, methanol, ethanol, isopropyl alcohol, glycerol, polyols, petrochemicals, co-precipitant solutions, crosslinking solutions, and combinations comprising one or more of the foregoing additives.

[0052] The reactions that can be performed by the disclosed INM and NM processes and apparatus are not par-
particularly limited and include, for example, hydrothermal reactions, sol-gel reactions, reflux reactions, and solid state preparations such as mixed solids. All of these reactions can be employed to produce metal-based catalysts for various processes.

When the reaction is a hydrothermal reaction, the first liquid precursor composition and the second liquid precursor composition may each comprise one or more metal precursors. The ultrafine material (e.g., catalyst precursor) produced may be calcined to obtain a metal oxide catalyst. For example, the first precursor liquid may comprise Mo, V, and Te precursors and the second precursor solution may comprise Nb and Pd precursors. The Mo—V—Te—Nb—Pd-oxide precursor produced may be calcined and employed as a catalyst for propane oxidation to form acrylic acid.

In another embodiment, the reaction is a sol-gel reaction. A “sol-gel technique” is a process wherein a free flowing fluid, “sol”, is first prepared by dissolving suitable precursor materials such as colloids, alkoxydes or metal salts in a solvent. The “sol” is then dosed with a reagent to initiate reactive polymerization of the precursor. A typical example is tetraethoxysilicate (TEOS) dissolved in ethanol. Water, with trace acid or base as catalyst to initiate hydrolysis, is added. As polymerization and crosslinking proceeds, the free flowing “sol” increases in viscosity and can eventually set to a rigid “gel”. In this embodiment, the first liquid precursor composition comprises, for example, a metal precursor solution and the second liquid precursor composition comprises a crosslinking agent.

An exemplary ultrafine material produced in a sol-gel reaction is a catalyst for the epoxidation of an alkene, whereby an oxygen atom is added to a carbon-carbon double bond to form an epoxide. Examples of epoxidation reactions include, but are not limited to, ethylene oxidation to ethylene oxide, propylene oxidation to propylene oxide, styrene oxidation to styrene oxide. Epoxides are important reactants for the manufacture of many commercial chemicals. Examples of products obtained from epoxides are: glycol and polyethylene glycol from ethylene oxide, propylene glycol from propylene oxide and phenylacetaldehyde from styrene oxide.

In this embodiment, the catalyst comprises a transition metal catalyst comprising, for example, manganese. In the reaction to form the catalyst in this example, the first liquid precursor composition comprises a manganese precursor and the second liquid precursor composition comprises a crosslinking agent. The product from this reaction could comprise a manganese oxide catalyst or a manganese catalyst precursor.

In another embodiment, the process includes a co-precipitation reaction. In one embodiment, the first liquid precursor composition comprises a metal precursor and the second liquid precursor composition comprises a co-precipitant. An exemplary application of a product of a co-precipitation reaction is as a catalyst for the production of hydrogen by methanol steam reforming. Catalysts comprising the base metals copper, zinc, aluminum, chromium, iron, cobalt and nickel, for example, may be employed for methanol reforming. In this embodiment, the first precursor liquid may comprise copper, zinc and aluminum precursors and the second precursor liquid may comprise a co-precipitant solution. An example of co-precipitant solution could be an aqueous solution of sodium hydroxide and sodium carbonate. The product formed is a Cu/Zn/AI oxide catalyst precursor. The catalyst forms after calcining the catalyst precursor at temperatures greater than 300°C.

The INM and NM processes and apparatus can be employed to produce a variety of sol-gel and solid materials that can be formed from liquid phase precursors. The ultrafine materials produced by the disclosed process and apparatus include, for example, metal oxides, mixed metal oxides, aluminosilicates, zeolites, ceramics, alloys, insulators, polymers that can be synthesized from liquid precursors, semiconductors, superconductors, clays, and the like. Catalyst supports such as alumina, silica, zeolites, or other materials that can be employed to hold active catalytic components can be produced.

The products can be highly dispersed metal oxides, that is, metal oxides that have a small particle size and a high surface area. It is also possible to produce highly dispersed metal crystallites on a support by the INM method. The dispersion (D) of a metal or metal oxide is defined by the fraction of the particular metal atom exposed to the surface. % D=(N_s/N_T)×100, where N_s is the number of surface atoms and N_T is the total number of atoms of the material. Dispersion is an important concept in heterogeneous catalysis, since atoms that are exposed to the surface are able to play a role in catalytic surface reactions. Dispersion increases with decreasing crystallite size and/or with increasing surface area. Mixed oxides are highly dispersed when the % dispersion is high. Dispersion can vary from 0% to 100%.

A mixed metal oxide may be, for example, a metal compound containing the elements A, M, N, X, and O. In one embodiment, A comprises Mo, W, Fe, Nb, Ta, Zr, Ru, and mixtures thereof; M comprises V, C, Cr, and mixtures thereof; N comprises Mo, W, and mixtures thereof; N comprises Fe, Ni, Pd, Pt, Br, Bi, B, In, Ce, and mixtures thereof. In one embodiment, A comprises Mo, W, and mixtures thereof; M comprises V, C, Cr, and mixtures thereof; N comprises Te, Bi, Sb, and mixtures thereof; and X comprises Nb, Ta, W, Ti, Al, Zr, Cr, Mn, Fe, Ru, Co, Rh, Ni, Pd, Pt, Br, Bi, B, In, Ce, and mixtures thereof. In another embodiment, A is Mo, M is V, N is Te and X is Nb.

The disclosed method may be used to form various metals and alloys or composites thereof. For example, alloys including transition metals such as Cu, Ni, Co, Fe, Mn, or alloys or composites containing these metals, may be made. Further examples include Cr, Zn, Ga, Ru, Rh, Pd, Ag, Cd, Sn, Sb, W, Re, Ir, Pt, Au, and Pb. Still further examples are alloys of any of the above, such as, for example, CuNi, AgNi, FeCu, FePt, FeNi, FeCo, CuCo, and the like. Metal/ceramic composites are also possible.

An embodiment of an apparatus for the INM process is illustrated in FIG. 1. The first component is an in situ mixing setup (10), which is employed to inject simultaneously two liquid precursor compositions (A (11) and B (12)) connected, for example, by a T-connector (13). The flow of liquid precursor composition A (15) and the flow of liquid precursor composition B (16) may be controlled with a syringe pump (14). The flow of the mixed liquid precursors (17) is then directed to an atomizer (20). The continuous mixing setup (10) is in fluid communication with the atomizer (20).
The second component of the apparatus is an atomizer (20), such as an ultrasonic nozzle spray, which is employed to form droplets (e.g., spray effect) when a liquid (17) is injected through the feed tube (22) of the nozzle. The ultrasonic waves can be generated broadband ultrasonic generator (21). The droplets produced by the atomizer (20) are directed to the microwave chamber (30). The atomizer (20) is in fluid communication with the reaction chamber (30).

The third component is a reaction chamber (30) in communication with a volumetric heating source (31), which is used to irradiate the droplets formed by the atomizer (20) as they pass through the chamber (30). The product produced flows through a product collection device (32) and is cooled. In one embodiment, reaction chamber 30 is a microwave chamber and the volumetric heating source 31 is a microwave source.

An embodiment of a nozzle-microwave apparatus is illustrated in FIG. 2. The first component is an injection setup (100), which is employed to inject liquid precursor composition B (120) into the atomizer (200). The flow of liquid composition precursor B (160) may be controlled with a syringe pump (140). The flow of liquid precursor composition B (160) is then directed to an atomizer (200).

The second component is an atomizer (200), such as an ultrasonic nozzle spray, which is employed to form droplets (e.g., spray effect) when a liquid (160) is injected through the feed tube (210) of the nozzle. The ultrasonic waves can be generated broadband ultrasonic generator (220). The droplets produced by the atomizer (200) are directed to the microwave chamber (300) which comprises liquid precursor A. The atomizer (200) is in fluid communication with the microwave chamber (300).

The third component is a microwave chamber (300) in communication with a microwave source (310), which is used to irradiate the droplets formed by the atomizer (200) with microwaves as they pass through the chamber (300). In this embodiment, liquid precursor A is heated under microwaves in the microwave chamber (300) while liquid precursor B is atomized into the microwave chamber (300). The product produced flows through a product collection device (320) and is cooled.

The invention is further illustrated by the following non-limiting examples.

**EXAMPLES**

Materials for Control Example 1 and Example 1

**[0069]** (Mo, V, and Te-Nb-Oxalic acid: HNO₃ = 1.28:0.21:0.155:0.43)

**[0070]** Prepare solution A (Mo — V — Te): Use 35.366 g of ammonium molybdate (NH₄)₂MoO₄·4H₂O, dissolve in 200 ml DI H₂O using moderate heating 60°C during mixing. After the Mo completely dissolves, add 6.666 g ammonium metavannadate NH₄VO₃. After all NH₄VO₃ dissolves, then add telluric acid. Allow Te dissolve to form a homogeneous bright orange color solution. Then transfer the content to a volumetric flask and dilute the total volume to 240 cc with additional distilled H₂O.

**[0071]** Prepare solution B (Nb-Oxa-NO₃): Use 15.26 g of ammonium niobium oxalate (NH₄NbO(C₂O₄)₂·2H₂O, 20.7 wt % Nb), dissolve all then add 2.79 g of oxalic acid anhydride, 5.418 g HNO₃, mixed at room temperature and dilute it to 240 ml with additional distilled H₂O, then we get a colorless solution.

**Example 1**

Prepare Mo—V—Te—Nb-Ox Catalyst Precursor by the In-Situ Ultrasonic Nozzle Spray, Microwave Method

**[0072]** A Mo—V—Te—Nb-Ox catalyst precursor is prepared using in-situ nozzle mixing and microwaves (INM method). Using two 60 ml syringes, take solution A and B, respectively. Solution A and solution B are mixed in situ (at the ultrasonic nozzle) using two syringes, a “T” connector and a syringe pump. The mixture prepared in situ is then injected into the tubular reactor inside the microwave cavity using the nozzle spray, which allows the formation of small droplets. The droplets coming out of the nozzle spray can be described as follows: the droplets come out of the nozzle, go through the microwave cavity and then fall down outside of the cavity in a round bottom flask container. Ideally, solution A and B are injected into the nozzle substantially simultaneously. While A and B may not be injected into the nozzle at the exactly same time due to the inaccuracy of the instrument, the timing can be improved by mixing A and B at the “T” connector first then injecting the mixture to the nozzle.

**[0073]** After solutions A and B are injected into the nozzle, droplets formed are microwaved at 100 W. The final material is collected outside of the cavity of the microwave oven in round bottom flask. The material looked not totally gelled. It has an orange color gel with a bright orange color liquid. It is believed that this material may be a colloid.

**[0074]** The materials collected were dried in a rotavap apparatus. The rotation speed is 60 rpm. After drying at 60°C for about 2 hours, a bright orange color powder is obtained.

**Control Example 1**

Prepare Mo—V—Te—Nb-Ox Catalyst Precursor by the In-Situ Ultrasonic Nozzle Mixing

**[0075]** A Mo—V—Te—Nb catalyst is also prepared using the in-situ nozzle mixing method (IN). The first two steps are the same as INM method. In the third step, the in-situ mixing mechanism is followed by the ultrasonic nozzle step at room temperature, bypassing the microwave step. The gel collected exhibits a bright orange color.

**[0076]** The materials collected were dried in a rotavap apparatus. The rotation speed is 60 rpm. After drying at 60°C for about 2 hours, a bright orange color powder is obtained.

Materials for Control Example 2 and Example 2

**[0077]** Ammonium heptamolybdate, ammonium vanadate and telluric acid were used to prepare Solution A: 1 M Mo, 0.3 M V and 0.23 M Te. Niobium ammonium oxalate, oxalic acid dehydrate, palladium (II) nitrate hydrate, and nitric acid were used to prepare Solution B: 0.17 M Nb, 0.155 M oxalic acid.
acid, 0.24 M HNO₃ and 0.01 M Pd. Alternative sources for V and Te include vanadyl sulfate hydrate and tellurium oxide.

Control Example 2

A Mo—V—Te—Nb-Ox catalyst (Cat 1) was prepared using the catalyst preparation illustrated in FIG. 3 in which the solutions A and B are mixed in bulk inside the reactor (50). The bulk mixture was then irradiated with microwaves. The resulting gel was dried at room temperature. The dried sample was calcined under air at 25° C. to 275° C. at 10° C./min and held at 275° C. for 1 hour, and then under argon at 275° C. to 600° C. at 2° C./min and held at 600° C. for 2 hours.

Example 2

Preparation of Mo—V—Te—(X)-Ox Catalysts

The inventive procedure was used to prepare a Mo—V—Te—Nb-Ox catalyst (Cat 2). Cat 2 was prepared by using the INM method illustrated in FIG. 1 in which the solutions A and B were mixed in situ (10) (at the nozzle (20)) using two syringes (11, 12), a “T” connector (13) and a syringe pump (14). The in-situ-prepared mixture (17) was injected into the tubular reactor inside the microwave chamber (30) using the nozzle spray (20), which allows the formation of small droplets. The resulting gel was dried at room temperature. The dried sample was calcined under air at 25° C. to 275° C. at 10° C./min and held at 275° C. for 1 hour, and then under argon at 275° C. to 600° C. at 2° C./min and held at 600° C. for 2 hours.

Example 3 Alternate Preparation of Mo—V—Te—(X)-Ox Catalysts

Two solutions are prepared (1) Solution A: 1 M Mo+0.3 M V+0.23 M Te and (2) Solution B: 1 M HNO₃. Solution B is added from a nozzle located at the top of the reactor to Solution A located inside the microwave heating zone. This experimental design is shown in FIG. 2. Appropriate experimental conditions such as speed of injection of reactants and microwave power are adjusted to favor the formation of Mo—V—Te-Ox catalyst precursor. Precipitates formed are filtered, washed and dried at room temperature overnight. The dried material may be calcined as described in Example 2.

Example 4

Alternate Preparation of Mo—V—Te—(X)-Ox Catalysts

Two solutions are prepared (1) Solution A: 1 M Mo+0.3 M V+0.23 M Te and (2) Solution B: 1 M HNO₃. Then, solution A and solution B are mixed in situ and sprayed in the microwave chamber as described in Example 1. Appropriate experimental conditions such as speed of injection of reactants and microwave power are adjusted to favor the formation of Mo—V—Te-Ox catalyst precursor. The solids formed are filtered, washed and dried at room temperature overnight. The dried material may be calcined as described in Example 2.

Example 5

Preparation of CuO/ZnO/Al₂O₃ Catalysts

Copper (II) nitrate hemipentahydrate, zinc nitrate hexahydrate, aluminum nitrate nonahydrate are used to prepare Solution A: 0.2 M Cu(NO₃)₂.2.5H₂O+0.3 M Zn(NO₃)₂.6H₂O+0.05 M Al(NO₃)₃.9H₂O. Sodium hydroxide and carbonate are used to prepare the co-precipitant solution (Solution B): 1 M NaOH+0.15 M Na₂CO₃. Solution B is added from a nozzle located at the top of the reactor to Solution A located inside the microwave heating zone. This experimental design is shown in FIG. 2. Appropriate experimental conditions such as speed of injection of reactants and microwave power are adjusted to favor the formation of Cu—Zn—Al-Ox catalyst precursor. The solids formed are filtered, washed and dried at 80° C. overnight. The dried material may be calcined at temperatures greater than 300° C.

Example 6

Alternate Preparation of CuO/ZnO/Al₂O₃ Catalysts

Two aqueous solutions are prepared (1) Solution A: 0.02 M Cu(NO₃)₂.2.5H₂O+0.03 M Zn(NO₃)₂.6H₂O+0.005 M Al(NO₃)₃.9H₂O and (2) Solution B: 0.1 M NaOH+0.015 M Na₂CO₃ (co-precipitant solution). Then, solution A and solution B are mixed in situ and sprayed in the microwave chamber. Appropriate experimental conditions such as speed of injection of reactants and microwave power are adjusted to favor the formation of Cu—Zn—Al-Ox catalyst precursor. The solids formed are filtered, washed and dried at 80°
The dried material may be calcined at temperatures greater than 300° C.

Example 7
Preparation of MnOx Catalysts

Two aqueous solutions are prepared (1) Solution A: KMnO₄ in concentrations ranging from 0.2-0.4 M, and (2) Solution B: 1.4 M glucose. Solution B is added from a nozzle located at the top of the reactor to Solution A located inside the microwave heating zone. Appropriate experimental conditions such as speed of injection of reactants and microwave power are adjusted to favor the formation of MnOx catalyst. The solids formed are filtered, washed and dried at room temperature.

Example 8
Preparation of MnOx Catalysts

Two aqueous solutions are prepared (1) Solution A: KMnO₄ in concentrations ranging from 0.2-0.4 M, and (2) Solution B: 1.4 M glucose. Then, solution A and solution B are mixed in situ and sprayed in the microwave chamber. Appropriate experimental conditions such as speed of injection of reactants and microwave power are adjusted to favor the formation of MnOx catalyst. The solids formed are filtered, washed and dried at room temperature.

Example 9
Preparation of MnOx Catalysts

Two aqueous solutions are prepared (1) Solution A: KMnO₄ in concentrations ranging from 0.2-0.4 M, and (2) Solution B: MnSO₄.H₂O in concentrations ranging from 0.3-1.8 M. Solution B is added from a nozzle located at the top of the reactor to Solution A located inside the microwave heating zone. Appropriate experimental conditions such as speed of injection of reactants and microwave power are adjusted to favor the formation of MnOx catalyst. The solids formed are filtered, washed and dried at 120° C. overnight.

Example 10
Preparation of MnOx Catalysts

Two aqueous solutions are prepared (1) Solution A: KMnO₄ in concentrations ranging from 0.2-0.4 M, and (2) Solution B: MnSO₄.H₂O in concentrations ranging from 0.3-1.8 M. Then, solution A and solution B are mixed in situ and sprayed in the microwave chamber. Appropriate experimental conditions such as speed of injection of reactants and microwave power are adjusted to favor the formation of MnOx catalyst. The solids formed are filtered, washed and dried at 120° C. overnight.

Example 11
Preparation of Molecular Sieves (Zeolite-A)

Amorphous material was prepared by mixing 3.25 M sodium aluminate (Riedel-de Haën) with 1.2 M sodium hydroxide followed by addition of tetraethoxyxorsilicate (TEOS). The resulting solution was refluxed at 90° C. for 1.5 hours. The amorphous product was filtered, washed with distilled water and dried overnight at 80° C.

Crystallization of zeolite-A was achieved by obtaining 1.5 g of the as-prepared dried amorphous product mixed in 1.25 M sodium hydroxide or TMAOH, with or without seed and subjected to various variations of microwave power (0-300 W), with or without ultrasonic spray nozzle, and precursor flow rates. The synthesis tested was either continuous or non-continuous (conventional). The obtained product was washed with distilled water and dried overnight at 80° C.

When no microwaves and no ultrasonic spray nozzle were employed, the resulting material remained amorphous, but when ultrasonic nozzle was used and no microwaves the expected phases were present. In contrast when microwave radiation (100 W) was used and no nozzle, zeolite-A XRD peaks were present but with additional impurity peaks (hydroxyCeladonite).

 moreover, FESEM micrographs show that when the nozzle is used, well faceted cubic particles start to emerge.

FIGS. 9-11 shows that microwave power less 200 W resulted in pure and well defined zeolite-A cubic particles. FIG. 10 shows the XRD patterns when TMA⁺ was used instead of Na⁺. Not shown here, the FESEM showed rounded particles and no cubic particles were observed, of course NaOH is a strong electrolyte and absorbs the microwaves very well.

FIG. 13 shows the FESEM micrographs of zeolite-A prepared using a conventional hydrothermal non-continuous method at 80° C. for less than 30 minutes.

The particles here are different from those prepared by continuous nozzle method.

Continuous synthesis using both the microwave radiation and ultrasonic nozzle resulted to average crystallites size in the range of 25-180 nm as determined from X-ray diffraction data using Deybe-Scherrer formula.

The results clearly show that microwave radiation and ultrasonic nozzle do compliment each other in the discussed synthesis. Moreover, the ultrasonic nozzle alone resulted in crystallization of zeolite-A using a non-clear method of synthesis. In the continuous process with nozzle and microwave, the material was crystallized in less than 1 min.

Example 12
Continuous Synthesis of Nickel Ferrite

Nickel ferrite was synthesized by mixing nickel (II) and Iron (III) nitrate salts with distilled water in a ratio of 1:2. This solution was mixed and transferred in one 60 ml syringe. 0.6-1.2 M of NaOH and Na₂CO₃ was prepared and transferred in separate 60 ml syringes. In this case synthesis was done using a 120 kHz nozzle equipped with a dual feed system. The solution mixtures of the metal nitrates and either sodium hydroxide or sodium carbonate did not mix until they were simultaneously ultrasonically sprayed.

The resultant product was washed and dried overnight at room temperature. The samples were then thermally treated from 600-1000° C. for 1-4 hours.

Novel methods and apparatus for the production of ultrafine materials are described. The techniques are simple and can provide substantially uniform reaction conditions in
a continuous process, which gives the possibility of producing large batches of material for industrial testing applications. The materials produced advantageously have nanometer- and micrometer-sized grains and substantially uniform size distributions which can enhance their properties.

All ranges disclosed herein are inclusive and combinable. While the invention has been described with reference to exemplary embodiments, it will be understood by those skilled in the art that various changes may be made and equivalents may be substituted for elements thereof without departing from the scope of the invention. In addition, many modifications may be made to adapt a particular situation or material to the teachings of the invention without departing from the essential scope thereof. Therefore, it is intended that the invention not be limited to the particular embodiment disclosed as the best mode contemplated for carrying out this invention.

1. A process for forming an ultrafine material, comprising:
   mixing two or more liquid precursor compositions in a mixing apparatus to form a precursor mixture, wherein the mixing apparatus is in fluid communication with an atomizer;
   atomizing the precursor mixture in the atomizer to form droplets;
   directing the droplets to a reaction chamber in communication with a volumetric heating source, wherein the reaction chamber is in fluid communication with the atomizer;
   volumetrically heating the droplets to produce the ultrafine material; and
   isolating the ultrafine material.
2. The process of claim 1, wherein volumetrically heating comprises contacting the droplets with microwaves, radiofrequency waves, a plasma, an arc discharge, or laser irradiation.
3. The process of claim 2, wherein volumetrically heating comprises contacting the droplets with microwaves.
4. The process of claim 1, wherein the mixing apparatus comprises a micromixer.
5. The process of claim 1, wherein the mixing apparatus comprises a syringe pump and a T-connector.
6. The process of claim 1, wherein the atomizer comprises an ultrasonic nozzle.
7. The process of claim 1, wherein at least one of the liquid precursor compositions comprises a precursor molecule comprising a metal component.
8. The process of claim 7, wherein the metal component is aluminum, boron, tin, thallium, antimony, lithium, sodium, potassium, strontium, yttrium, zirconium, barium, titanium, lead, samarium, rubidium, lanthanum, indium, nickel, copper, cobalt, calcium, magnesium, manganese, bismuth, zinc, silicon, germanium, nickel, astatine, tantalum, vanadium, iron, chromium, cadmium, molybdenum, antimony, cesium, gallium, niobium, silver, selenium, tungsten, tellurium, thorium, palladium, arsenic, platinum, rhodium, ruthenium, uranium gold, silver, or a combination comprising one or more of the foregoing metal components.
9. The process of claim 7, wherein the precursor molecule comprises an anion, wherein the anion is hydroxide, nitrate, sulfate, carbonate, phosphate, chloride, halide, acetate, oxalate, acety acetate, ammonia, amine, silicate, selenite, sulfate, nitrite, and combinations comprising one or more of the foregoing anions.
10. The process of claim 7, wherein the metal component is in the form of an organometallic compound.
11. The process of claim 1, wherein the ultrafine material has maximum diameters of about 1 nanometer to about 100 micrometers.
12. The process of claim 1, wherein the ultrafine material is a metal oxide, a mixed metal oxide, an aluminosilicate, a zeolite, a ceramic, an alloy, an insulator, a polymer, a semiconductor, a superconductor, a clay, alumina, or silica.
13. The process of claim 3, further comprising inducing a plasma in the reaction chamber during the contacting.
14. The process of claim 1, comprising treating the ultrafine material with a thermal heating source prior to isolating the material.
15. An apparatus for forming an ultrafine material, comprising:
   a mixing apparatus to form a mixture of two or more precursor liquids;
   an atomizer for forming droplets of the mixture; and
   a reaction chamber in communication with a volumetric heating source to irradiate the droplets formed by the atomizer;
   whereby the mixing apparatus and the atomizer are in fluid communication, and the atomizer and the reaction chamber are in fluid communication.
16. The apparatus of claim 15, wherein the volumetric heating source comprises a pulsed wave laser source, a continuous wave laser source, a flashlamp or filament lamp, a radiofrequency source, a microwave source, an ac discharge source, a dc discharge source, or a corona discharge source.
17. The apparatus of claim 15, wherein the mixing apparatus comprises a micromixer.
18. The apparatus of claim 15, wherein the mixing apparatus comprises a syringe pump and a T-connector.
19. The apparatus of claim 15, wherein the atomizer comprises an ultrasonic nozzle.
20. A process for forming an ultrafine material, comprising:
   atomizing a first liquid precursor in an atomizer to form droplets;
   directing the droplets to a reaction chamber in communication with a volumetric heating source, wherein the reaction chamber is in fluid communication with the atomizer, and wherein the reaction chamber comprises a second liquid precursor;
   volumetrically heating the first and second precursors to produce the ultrafine material; and
   isolating the ultrafine material.