Heterobimetallic mixed metal oxide (HMMO) nanoparticles and their applications

Pramesh N. Kapoor*a, Harish K. Sharmab, Ajay K. Bhagia and Malti Sharma*e

aChemistry Department, Delhi University, Delhi-110 007, India
E-mail: prameshn@yahoo.com; pnkapoor@himalaya.du.ac.in
bChemistry Department, Kurukshetra University, Kurukshetra-136 119, India

The chemistry of HMMO (heterobimetallic mixed metal oxide) nanoparticles of the type ABO3 (perovskite), AB2O4 (spinel and antisperi) and AB2O3 (pseudobrookite) has been discussed. Their preparation by the sol-gel route using mixtures of alkoxides, heterobimetallic alkoxides and heterobimetallic-μ-oxo alkoxides are described. Physical and chemical properties, with special reference to high surface area, morphology, crystal structure, catalysis and destructive adsorption studies, along with some important applications have also been discussed.

Developments in the field of HMMO nanoparticles have produced very significant and interesting results, which are evident from the recent reports published1-5 in the literature. HMMO nanoparticles exhibit a wide array of unusual properties and can be considered as new materials that bridge molecular and condensed matter. One of the unusual features is their enhanced surface chemical reactivity towards incoming adsorbates6-8 and chemical warfare agents9,10. For example, Al2O3/MgO HMMO nanoparticles adsorb SO2 and CCl4, and MgAl2O4 adsorbs and destroys paraxon [diethyl-4-nitrophenol phosphate (DNPP)]11 more efficiently as compared to commercially prepared and pure MgO and Al2O3 nanoparticles. This enhanced surface reactivity is attributed to the presence of high concentration of edge/corner sites and other defects, which makes HMMO nanoparticles co-ordinatively unsaturated. Furthermore, the presence of two different metal centres in HMMOs increases their efficiency, due to the close proximity of acidic and basic centres.

In short, the following factors are considered to be important for the unusual chemical properties of HMMO nanoparticles: (i) acid-base behaviour, (ii) high surface area (due to the small particle size with dimensions in the range 1-10 nm), (iii) several types of deficiencies in the bulk as well as on the surface. The above stated properties make these HMMO nanoparticles the best candidates for catalysis12-18 (both as catalysts and catalytic supports) and destructive adsorption6-8.

HMMO nanoparticle systems have been given special attention because of their unique size dependent properties, such as optical, electronic, and magnetic, in comparison to normal HMMOs. Semimagnetic semiconductors of nanometer-sized crystallites are expected to be influenced by the quantum confinement of the electronic states and have great potential for a variety of applications due to the unique properties of quantum dots3.

The synthesis of HMMO nanoparticles by the conventional method is based on solid-state reaction19, which requires repeated cycles of milling and calcination at high temperature. This results in lack of homogeneity (due to incomplete reaction) and low surface area (~1 m2/g). In contrast to the solid-state method, various other physical and chemical methods are preferred. Physical methods include gas condensation techniques20-22, spray pyrolysis23-24, thermochromatic decomposition of metal-organic precursors in flame reactors25, and some other aerosol processes named according to the energy sources applied to reach the required temperatures during gas-particle conversion. The wet chemical methods include the sol-gel method, reverse microemulsion technique26-28 and precipitation from solution29,30. It has been observed that, out of the various physical and chemical methods, the sol-gel method assumes special significance for the preparation of more homogeneous nanosized HMMOs of high purity and surface area.

A survey of the literature shows that sol-gel31-37 processing has several advantages over other techniques for synthesizing nanopowders of mixed metal oxide ceramics. These include (i) the production of ultrafine porous powders, (ii) the homogeneity of the product as a result of homogeneous mixing of the starting materials at the molecular level and (iii) the possibility of obtaining the ceramic material in different forms by controlling the conditions. In

1Professor S. S. Sandhu Lecture (2001) delivered under the auspices of Indian Chemical Society on 24 December 2003 at Jhansi, Uttar Pradesh.
this process, a colloidal sol is converted into a gel by ageing. The gel is subsequently calcined by special techniques, giving rise to a crystalline product with homogeneous composition and large surface area.

In view of the solubility of metal alkoxides and oxoalkoxides in organic solvents, these materials are strongly preferred as precursors in sol-gel processes. In heterobimetallic-µ-oxo alkoxides, $\text{M-O-M'}$ linkage is present, which makes the $\text{M-O-M'}$ bond strong and stable as compared to other precursors. Non-cleavage of the $\text{M-O-M'}$ bond, even upon hydrolysis followed by dehydration (drying), makes homogeneous oxides of high surface area HMMO nanoparticles. Interestingly, the structural relationship among these precursors, coupled with their versatility towards hydrolysis, led to their increasing use as starting compounds. These compounds are considered as especially suitable precursors over other precursors such as metal nitrates, acetates, monodispersed metal hydrous oxides, mainly due to the ease of their purification (either by distillation or recrystallization), solubility in organic solvents, and their extremely facile hydrolyzability.

This article describes the synthesis of HMMO nanoparticles (perovskite, spinel and pseudobrookite) using either mixtures of metal alkoxides, heterobimetallic alkoxides or heterobimetallic-µ-oxo alkoxides as precursors by the sol-gel method. Other methods of the preparation, and composite/doped nanoparticles are not being covered.

The sol-gel route can be considered as a two-step inorganic polymerization.

(i) Hydrolysis of metal alkoxides: In this step, polymerization starts by hydrolysis at the metal-alkoxy linkage yielding alcohol and a new reactant containing hydroxylated metal centres ($\text{M-OH}$).

$$\text{M(OR)}_n + x \text{H}_2\text{O} \rightarrow [\text{M(OR)}_n-x(\text{OH})_x] + x \text{ROH}$$

(ii) Condensation: In this step, three-dimensional propagation occurs when hydroxylated species condense to form oxopolymers by the combination of the following steps.

$$\text{MOH} + \text{MOR} \rightarrow \text{M-O-M} + \text{ROH} \text{ (alkoxolation)}$$

$$\text{MOH} + \text{MOH} \rightarrow \text{M-O-M} + \text{H}_2\text{O} \text{ (oxolation)}$$

$$\text{M(OH)}_2 + \text{MOR} \rightarrow (\text{HO})\text{M-O-M+ ROH} \text{ (olation)}$$

The nature of the inorganic framework depends upon the relative rates of hydrolysis and condensation at different centres. The rate of hydrolysis depends upon the nature of the metal in terms of its electrophilicity and ability to expand its co-ordination number. The hydrolysis rates of transition metal alkoxides (especially in the case of heterobimetallic alkoxides) are very high due to their highly electrophilic nature and ability to expand their coordination number. This sometimes complicates the problem by causing phase segregation and, to overcome this problem, a modified precursor is prepared by reacting the alkoxide with other ligands. This results in a new precursor, which may undergo hydrolysis at a slower rate. Finally, the solvent is removed from the gel. The manner in which the liquid phase is removed from the wet gel determines whether the dried material is a highly porous aerogel or a denser xerogel. Xerogel is formed as the solvent from wet gel evaporates resulting in a collapse of the wet gel structure. In case the network is compliant, the gel deforms due to the capillary forces generated by the liquid phase as it recedes into the body of the gel. Aerogel is actually a nanoscale mesoporous material of low density and high surface area, which results from supercritical drying (SCD) or ambient pressure methods upon wet gels.

Structure and morphology of HMMO nanoparticles

HMMO nanoparticles are known to have different structure and morphology, depending upon the size and charge of the constituent ions. The nature of these ions determines the final geometry adopted. HMMO nanoparticles prepared by the sol-gel method most often adopt one of the perovskite, spinel and pseudobrookite types of structures.

Perovskite structure (ABO$_3$ type)

HMMOs having the formula ABO$_3$ are called perovskite, e.g., CaTiO$_3$, SrTiO$_3$, BaTiO$_3$, etc. HMMOs of the type SrTiO$_3$ and BaTiO$_3$ have been prepared by reacting both the alkoxides in a 1 : 1 molar ratio by the sol-gel method, shown in Scheme 1. CaTiO$_3$ has been prepared from calcium acetate and titanium isopropoxide in 1 : 1 molar ratio and calcinations of the gel powder in air at temperatures upto 900°.

Recently, translucent BaTiO$_3$ and GdFeO$_3$ have been prepared by the sol-gel method using metal alkoxides in 1 : 1 molar ratio, followed by calcination at higher temperature (600–1100°).

The XRD pattern (Fig. 1) of SrTiO$_3$ in different solvents shows that it is an amorphous powder in ethanol. Furthermore, comparison of the XRD patterns of HMMO perovskites of the type SrTiO$_3$, BaTiO$_3$ and CaTiO$_3$, after calcination at different temperatures, suggests that calcination at 500° under pressure for SrTiO$_3$ and BaTiO$_3$, and at 900° in air for CaTiO$_3$, results in the appearance of an intense peak, indicative of high surface/volume ratio.
Kapoor et al.: Heterobimetallic mixed metal oxide (HMMO) nanoparticles and their applications

Scheme 1. Preparation route of perovskite SrTiO$_3$ or BaTiO$_3$.

Surface area analyses of these perovskites are given in Tables 1–3, which suggest that HMMO perovskites prepared by the sol-gel process have high surface area as compared to commercially available samples.

![Fig. 1. XRD patterns for synthesis of SrTiO$_3$ with different alcohols.](image)

Transmission electron microscopy (TEM) micrograph of SrTiO$_3$ (Fig. 2) indicates that it has a crystallite size of 10 nm, when calcined at 500°.

![Fig. 2. TEM of SrTiO$_3$ aerogel calcined at 500°.](image)

Table 1. Surface area of perovskites

| HMMO   | S.A. of HMMO prepd. by S-G (m$^2$/g$^{-1}$) | Commercial HMMO (m$^2$/g$^{-1}$) |
|--------|------------------------------------------|----------------------------------|
| CaTiO$_3$ | 21                                       | –                                |
| SrTiO$_3$ | 159                                      | 17                               |
| BaTiO$_3$ | 175                                      | 20–30                            |

Table 2. Aerogel SrTiO$_3$ (ethanol calcined) at different temperatures

| Conditions °C | Crystallite sizes, nm | Surface area m$^2$/g$^{-1}$ | Pore volume cc/g | Average pore size, Å |
|---------------|-----------------------|-----------------------------|-----------------|----------------------|
| 200           | 8                     | 159                         | 0.617           | 155                  |
| 300           | 6                     | 156                         | 0.571           | 145                  |
| 400           | 9                     | 114                         | 0.544           | 190                  |
| 500           | 10                    | 93                          | 0.453           | 194                  |

Table 3. Aerogel BaTiO$_3$ (ethanol isopropanol) at different temperatures

| Conditions °C | Surface area m$^2$/g$^{-1}$ | Total pore volume, cc/g | Avg pore size (d), Å |
|---------------|-----------------------------|-------------------------|----------------------|
| 300           | 175                         | 0.434                   | 101.7                |
| 400           | 89                          | 0.368                   | 165                  |
| 500           | 45                          | 0.391                   | 345.7                |

The structure of the perovskite phase was first thought to be cubic, but later confirmed as orthorhombic. The truly cubic form is referred to as "ideal perovskite", having a unit cell edge of ~4 Å containing one ABO$_3$. In this phase, the large cation A is surrounded by 12 oxide ions to form cuboctahedral co-ordination, whereas the B cation is surrounded by 6 oxide ions in an octahedral co-ordination.

The combination of high surface areas and nanosizes of aerogel SrTiO$_3$ and BaTiO$_3$ mixed oxides gives significant advantages in different applications, which are currently being explored.

Spinel structure (AB$_2$O$_4$ type)

It consists of a face-centered cubic arrangement of oxygen ions. A unit cell contains 32 O$^{2-}$ ions, 64 tetrahedral and 32 octahedral sites, which are occupied by A$^{2+}$ (A = Mg, Fe, Ca, Zn, etc.) and B$^{3+}$ (B = Al, Fe, etc.) cations, respectively. The general formula of the spinel is written as

$$
\text{A}_2\text{B}_2\text{O}_4
$$
$A^{II}B^{III}O_4$ [where $A^{II}$ is a group 2 metal ion or transition metal in the +2 oxidation state and $B^{III}$ is a Group 13 (B, Al, Ga, In) cation or transition metal ion in the +3 oxidation state]. MgAl$_2$O$_4$, CaAl$_2$O$_4$, MnAl$_2$O$_4$, FeAl$_2$O$_4$, CoAl$_2$O$_4$, NiAl$_2$O$_4$, ZnAl$_2$O$_4$, etc., were successfully prepared by Kapoor et al. [51]. Recently, ZnAl$_2$O$_4$ has also been prepared from the heterobimetallic alkoxide via the sol-gel method followed by calcination at 400°C. This is a very stable type of HMMO, prepared by the sol-gel technique shown in Scheme 2.

![Scheme 2. Preparation route of spinel MgAl$_2$O$_4$.](image)

The XRD pattern (Fig. 3a) of MgAl$_2$O$_4$ shows that it is spinel at ~500°C, but on increasing the temperature, the intensity of the peak increases, which suggests that the size of the particle decreases. Furthermore, the XRD patterns (Fig. 3b) for MAI$_2$O$_4$ (where M = Fe, Co, Zn) were examined by Kapoor et al. [51], and compared with the XRD pattern of MgAl$_2$O$_4$, which shows superimposability, suggesting their spinel structure.

![Fig. 3(a). XRD of MgAl$_2$O$_4$.](image)

![Fig. 3(b). XRD of ZnAl$_2$O$_4$: (a) as synthesized and (b) after heat treatment at 500°C for 1 h.](image)

Surface area analyses (Table 4) show that Mg-O-Al, prepared by the oxo bridge method has the highest surface area up to 440 m$^2$g$^{-1}$ and 470 m$^2$g$^{-1}$ after heat treatment at 500°C in vacuum. However, Mg-O-Al, when prepared by the bridged alkoxide method, shows surface areas of only 228 m$^2$g$^{-1}$ and 242 m$^2$g$^{-1}$ after heat treatment. These results reflect the advantages of the method utilizing the oxo-bridged precursors to obtain high surface area homogeneous HMMO nanoparticles. Analogous Zn-O-Al, Fe-O-Al, Co-O-Al and Mn-O-Al surface areas were in the range of 310–340 m$^2$g$^{-1}$. TEM studies (Fig. 4) of spinels suggest their crystallite sizes.

| MAI$_2$O$_4$ | S.A. (m$^2$g$^{-1}$) after SCD | S.A. (m$^2$g$^{-1}$) after heat treatment at 500°C under vacuum |
|------------|---------------------------|----------------------------------|
| M = Mg     | 228                       | 242                              |
| M = Ca     | 260                       | 155                              |
| M = Zn     | 320                       | 340                              |
| M = Co     | 330                       | 315                              |
| M = Fe     | 320                       | 310                              |
| M = Mn     | 320                       | 308                              |

Solid state $^{27}$Al NMR (Fig. 5 and Table 5) is a good tool for analyzing the co-ordination environment of Al$^{3+}$ ions, in particular the octahedral to tetrahedral ratio, and their existence. When A$^{2+}$ ions occupy one eighth of the tetrahedral holes and B$^{3+}$ ions half the octahedral holes, the structure is called "normal" spinel. It is a stable arrangement having tetrahedral arrangement about a divalent cat-
sites are occupied by half of the $B^{3+}$ ions, whereas the rest of the $B^{3+}$ ions, along with the $A^{2+}$ ions, occupy half of the octahedral sites. The general formula for "normal" spinel is written as $(A)[B_2O_4$, while for "inverse" spinel, it is $(B)[AB]O_4$, where $()$ and $[]$ represent tetrahedral and octahedral arrangements. Many MMOs have intermediate cation ratios, and the general formula of these structures is written as $(A_{1-x}B_x)[B_{2-x}A_x]O_4$, where $x$ is the "inversion parameter" ($0 < x < 1$).

Pseudobrookite structure (AB$_2$O$_5$ type)

HMMOs of this type have the general formula AB$_2$O$_5$. Pseudobrookite is a rare oxide mineral and provides this type of structure for a variety of minerals and synthetic phases. The mineral name derives from its appearance. Pseudobrookite resembles brookite, one of the titanium dioxide polymorphs. The synthetic phase "Karrooite" MgTi$_2$O$_5$ also has the pseudobrookite structure in which both the metal ions are coordinated by six oxygens, e.g., MgTi$_2$O$_5$\textsuperscript{53}, FeTi$_2$O$_5$\textsuperscript{54}, etc.

All these pseudobrookite phases are metastable at RT. Stability at high temperature has been proposed to result from the mixing of cations between two different cation-oxygen octahedra, which are connected by shared edges.

This phase (MTi$_2$O$_5$) is readily converted into rutile or anatase TiO$_2$, and perovskite structure MTiO$_3$. Only few HMMOs of this class are known; other pseudobrookites such as AB$_2$O$_5$ (M = Ca, Mn, Zn; $M'$ = Ti)\textsuperscript{55} have been prepared and further studies are going on.

MgTi$_2$O$_5$ has been successfully prepared\textsuperscript{55} by the sol-gel method, which is shown in Scheme 3. Comparison of the XRD pattern (Fig. 6) for MgTi$_2$O$_5$ prepared\textsuperscript{55} by the

![Scheme 3. Preparation route of pseudobrookite MgTi$_2$O$_5$.](image)

In some cases, e.g. NiFe$_2$O$_4$, one half of the $B^{3+}$ ions exchange their positions with $A^{2+}$ ions. This is called "inverse" spinel. In this arrangement, one eighth of tetrahedral

![Fig. 4. (a) TEM micrograph of the ZnAl$_2$O$_4$ material, after 500° heat treatment under vacuum, (b) high resolution TEM with SAD pattern shown in the inset.](image)

![Fig. 5. $^{27}$Al NMR of MAI$_2$O$_4$: (a) CaAl$_2$O$_4$, (b) MgAl$_2$O$_4$, (c) ZnAl$_2$O$_4$, (d) MgAl$_2$O$_4$(Mg-OR-Al).](image)

| Sample     | Peak position (δ) | Oh : Td ratio |
|------------|-------------------|---------------|
| MgAl$_2$O$_4$ | 9.7               | 70            | 74 : 26        |
| ZnAl$_2$O$_4$ | 9.7               | 66            | 85 : 15        |
| CaAl$_2$O$_4$ | 8.7               | 70            | 47 : 53        |

Table 5. $^{27}$Al solid-state MAS NMR spectra
sol-gel process with that of MgTi$_2$O$_5$ prepared by heating MgO and TiO$_2$ high temperature in a 1 : 2 molar ratio, exhibits superimposable pattern, showing their similar structures.

![Graph](image)

**Fig. 6. XRD pattern of MgTi$_2$O$_5$.**

**Properties and applications**

The properties of HMMO nanoparticles are size dependent. They exhibit unique chemical and physical properties that are remarkably different from those of the corresponding bulk materials. As the particle size decreases, the percentage of atoms residing on the surface increases, giving high surface to volume ratios. This allows more reactive centres becoming available for reactions to occur.

A variety of important aspects centre around the unusual chemical properties of HMMO nanoparticles; some of these are described below:

1. **As destructive adsorbents:**

   The development of novel methods for the disposal of chlorinated wastes and other toxic gases in the environment, from industries as well as other sources, has become a very urgent task. Recent studies have shown that HMMO nanoparticles attract significant attention as effective chemisorbents for such toxic gases as well as chlorine and phosphorus containing compounds.

   For this purpose, HMMOs play an important role. For example, Al$_2$O$_3$/MgO adsorbs SO$_2$, CCl$_4$ and paraxon more efficiently as compared to pure Al$_2$O$_3$ and MgO nanoparticles and commercially available oxides.

   $$2 \text{MgO} + \text{CCl}_4 \rightarrow 2 \text{MgCl}_2 + \text{CO}_2 \uparrow$$

   Adsorption of SO$_2$ was carried out with pure MgO, Al$_2$O$_3$ and mixed oxide Al$_2$O$_3$/MgO and compared. The experimental results showed that, at atmospheric pressure and RT, the SO$_2$ adsorbed onto Al$_2$O$_3$ nanoparticles was 3.5 molecules of SO$_2$/nm$^2$, on MgO nanoparticles it was 0.68 molecules of SO$_2$/nm$^2$, but the Al$_2$O$_3$/MgO MMO nanoparticles layer adsorbed 6.8 molecules of SO$_2$/nm$^2$.

   These data indicate that Al$_2$O$_3$/MgO efficiently adsorbs SO$_2$ in slightly more than one layer. This is probably due to the greater Lewis basicity of the MgO present and large surface area of Al$_2$O$_3$, which is beneficial for the adsorption of the acid gas.

   In the last few decades, pollution by diesel-engine exhausts has become an ever-increasingly serious problem. Soot and NO$_x$ are the main components to be removed from diesel exhaust. Among bimetallic spinel type oxides, CuFe$_2$O$_4$ may be useful, which shows intermediate activity and exceptionally high and low selectivity, respectively, to N$_2$ and N$_2$O formation$^{56}$.

   The most interesting application of HMMO spinels is for adsorbing paraxon$^{11}$. These particles possess their destructive adsorption ability due to the presence of acidic and basic oxides in one intermingled mixed metal oxide. HMMO nanoparticles, such as MAI$_2$O$_4$ (M = Mg, Ca, Sr, Ba) have been used for this purpose. To compare the relative adsorption efficiencies of various MMOS, 16 μL of paraxon and 100 mg of adsorbent were used. The results (Figs. 7 and 8) show that both MgAl$_2$O$_4$ and CaAl$_2$O$_4$ destructively adsorbed all 8 μL, whereas SrAl$_2$O$_4$ and BaAl$_2$O$_4$ were only able to destructively adsorb 6 μL before their surface became saturated. Therefore, HMMO systems of MgAl$_2$O$_4$ and CaAl$_2$O$_4$ are better at destructively adsorbing paraxon than SrAl$_2$O$_4$, BaAl$_2$O$_4$, pure MgO, CaO and Al$_2$O$_3$ nanoparticles. Another HMMO nanoparticle, SrTiO$_3$ is photoactive$^{48}$ under UV light and is able to decompose organic volatile compounds like acetaldehyde.

![Graph](image)

**Fig. 7. Reaction of AP-MgAl$_2$O$_4$ with paraxon (16 μL) after 20 min.**

2. **In catalysis:**

   Relatively little work has been reported where these nanostructured materials have been explored in classical catalytic processes. Some examples are given below.
In CuMn$_2$O$_4$, the Cu-Mn-O system is a well-known oxidation catalyst$^{57}$ for carbon monoxide oxidation with oxygen at RT. The activity of CuMn$_2$O$_4$ decreases at temperatures above 600° due to the crystallization of spinel CuMn$_2$O$_4$. The high activity of CuMn$_2$O$_4$ is believed to be due to the redox system Cu$^{2+}$ + Mn$^{3+}$ $\leftrightarrow$ Cu$^+$ + Mn$^{4+}$ and unique adsorption properties of carbon monoxide on Cu$^{2+}$/Mn$^{3+}$ as well as O$_2$ on Cu$^+$/Mn$^{3+}$. Similarly, NiMn$_2$O$_4$ and CuCo$_2$O$_4$ also have high activity.

It is clear that surface properties such as the precise surface structures and the role of point defects are crucial to the proper understanding of the catalytic$^{56}$ and electrochemical properties. La$_2$NiO$_4$ has been widely studied for its catalytic properties such as partial oxidation and hypochlorite decomposition. There is continuing interest in La$_2$CuO$_4$ since it also exhibits catalytic properties. It is used in several chemical reactions$^{59-61}$ including CO oxidation, NO reduction, CH$_4$ oxidation and as a three-way automobile exhaust catalyst$^{61}$.

Besides these applications, MAI$_2$O$_4$ (Ca, Sr, Ba)$^{62}$ have been widely used as hosts for ceramic pigments, practical phosphors and excitation sources for other phosphors and luminous paints.

Recently, Co-Ti pseudobrookite (uncalcined) oxide nanoparticles$^{55}$ were found to be good photocatalysts for the decomposition of acetaldehyde to carbon dioxide.

(3) In electronics, magnetics and optics:

HMMO nanoparticles are characterized by an ultrafine grain size (<50 nm). These particles are subjects of current interest because of their unusual magnetic, optical and electronic properties, which often differ from their bulk properties. The reasons for these are the confinement of electronic and vibrational excitation, quantum size effect and large surface to volume ratio. Perovskite type oxides of the general formula ABO$_3$ are important in materials science, physics and earth sciences, e.g., for their electrical properties. These are widely used for the preparation of electronic components, electro-optical and photocatalytic materials. For example, SrTiO$_3$, BaTiO$_3$ and related compounds have been extensively used in the preparation of high dielectric constant capacitors, PTC resistors, transducers and ferroelectric memories.

LaGeO$_3$ and La$_2$NiO$_4$ are of current interest due to their potential applications in solid oxide fuel cells and ceramic membranes for oxygen separation. The LiM$_2$O$_4$ type of spinels is also important. LiTi$_2$O$_4$ was the first oxide superconductor with a transition temperature exceeding 10 K. LiV$_2$O$_4$ showed all the characteristics of a heavy fermion system with an effective mass enhancement of the order of 100. Similarly, LiMn$_2$O$_4$ a very important positive electrode material for commercial Li-ion batteries.

ZnFe$_2$O$_4$ is well known as an anomalous antiferromagnetic substance. Recent studies have shown that ZnFe$_2$O$_4$, especially nanometer-sized nanoparticles, with a relatively small band gap, is a potentially useful solar energy material for photoelectric conversion and photochemical hydrogen production from water$^{63}$. It has the advantage of absorbing visible light, without being sensitive to photoanodic corrosion.

Conclusion

The above brief account clearly depicts a versatile fast developing chemistry of HMMO nanoparticles, which is many a time being triggered by the multifaceted demands for advanced oxide-ceramics with novel applications. These HMMOs, prepared by the sol-gel process, are nanoparticles of ultrafine purity and high surface area. This high surface area is responsible for their applications in destructive adsorption, catalysis, and other applications, such as in magnetics, optics and electronics.

Besides the above applications, metal oxide nanoparticles have either been used or tested for their applications in the following fields:

(1) Decontamination of chemical warfare agents (CWAs): CWAs are generally organophosphorus esters, e.g., nerve agents (also called "Soman") and blister agents (also called "mustard"). Nerve agents can react with the enzyme acetylcholinesterase, which inhibits its control over the central nervous system. Reaction of the CWAs on MgO, CuO or Al$_2$O$_3$ nanoparticles at RT decontaminates$^{10}$ them by the cleavage of the P-O and P-F bonds and make them nontoxic.
(2) Biocidal activity: Some nanomaterials possess biocidal activity towards spores and vegetative cells, viruses and toxins. For this purpose, CaO and MgO nanoparticles are generally used. MgO nanoparticles adsorb chlorine to form deep yellow adduct MgOCl₂ nanoparticles. This adduct is capable of oxidizing bacteria. This killing action is not well understood, but may be due to a combination of the abrasive nature of the MgO nanoparticles and oxidizing ability of the surface chlorine.

(3) Cosmetics: TiO₂ and ZnO nanoparticles have been used in sunscreen creams for protection against UV irradiation.

(4) Pharmaceuticals: They are also used as drug delivery agents. Nanoparticles have been developed that can safely cross the blood-brain barrier and deliver therapeutic agents to particular parts of the brain. Silica coated semiconductor nanoparticles are readily incorporated into a wide variety of eukaryotic cells.

(5) Nanotechnology: It is the science of building machines and materials at the molecular level, where key components are measured in nanometers. This promises medical advances, smarter and lighter materials, more efficient manufacturing, cleaner energy, faster and more efficient electronics and better ways to detect, prevent and treat pollution.

In light of the extensive studies and probable applications of HMMOs, they may prove to be the materials of this century.

References

1. A Khaleel, K. J. Klabunde and D. Park, High-Temp. Mater. Sci., 1995, 33, 99.
2. K. J. Klabunde and C. Mobs, in 'Chemistry of Advanced Materials', Wiley, New York, 1998.
3. K. J. Klabunde in 'Nanoscale Materials in Chemistry', Wiley, New York, 2001.
4. S. P. Decker, J. S. Klabunde, A. Khaleel and K. J. Klabunde, Environ. Sci. Technol., 2002, 36, 762.
5. P. N. Kapoor, A. K. Bhagi, R. S. Mulukutla and K. J. Klabunde, 'Ency. Nanosci. Tech.', Marcel Dekker, New York, 2004.
6. E. Lucas, S. Decker, A. Khaleel, A. Seitz, S. Fultz, A Ponce, W. Li, C. L. Carnes and K. J. Klabunde, Chem. Eur., 2001, 7, 2505; A Khaleel, P. N. Kapoor and K. J. Klabunde, Nanostruct. Mater., 1999, 11, 459.
7. S. Decker, I. Lagadic, K. J. Klabunde, J. Moscovici and A. Michalowicz, Chem. Mater., 1998, 10, 674.
8. C. L. Carnes, P. N. Kapoor, K. J. Klabunde and J. Bonevich, Chem. Mater., 2002, 14, 2922.
9. G. W. Wagner, P. W. Bartram, O. Koper and K. J. Klabunde, J. Phys. Chem. (B), 1999, 103, 3225.
10. G. W. Wagner, L. R. Procell, R. J. O'Connor, S. Munavalli, C. L. Carnes, P. N. Kapoor and K. J. Klabunde, J. Am. Chem. Soc., 2001, 123, 1636.
11. G. M. Medine and K. J. Klabunde in "Symposium on Nanotechnology and Its Potential Role in Homeland Security", Kansas State University, U.S.A., 2003, p. 22.
12. D. Kiessling, G. Went, K. Hagenau and R. Schoellner, Appl. Catal., 1991, 71, 69.
13. B. N. Reddy and M. Subrahmanyan, Langmuir, 1992, 8, 2072.
14. A. Corma, Chem. Rev., 1995, 95, 559.
15. N. Sun and K. J. Klabunde. J. Catal., 1999, 185, 506.
16. D. Heinz, W. F. Hoelderich, S. Krill, W. Boeck and K. Huthmacher, J. Catal., 2000, 192, 1.
17. H. Watanabe and Y. Koyasu, Appl. Catal., 2000, 194, 479.
18. C. L. Carnes and K. J. Klabunde, J. Mol. Catal., 2003, 194, 227.
19. A Bauger, J. C. Moutin and J. C. Niepce, J. Mater. Sci., 1983, 18, 3041.
20. M. S. El. Shall, W. Slack, W. Vann, D. Kane and D. Hanley, J. Phys Chem., 1994, 98, 3067.
21. A. S. Edelstein, G. C. Hadjipanayis and R. W. Siegel in "Nanophase Materials", Kluwer Academic Publisher, 1994, pp.73-80, 85-88.
22. G. M. Cow and K. E. Gonsalves in "Nanotechnology, Molecularly Designed Materials", American Chemical Society, Washington, 1996, pp.79-99.
23. T. T. Kodas, Adv. Mater., 1989, 6, 180.
24. G. L. Messing, S. C. Zhang and G. V. Jayanthi, J. Am. Ceram. Soc., 1993, 76, 2707.
25. G. Sksnndan, Y. I. Chen, N. Glumac and B. H. Karp, Nanostruct. Mater., 1999, 11, 149.
26. L. M. Gan, L. S. Zhang, H. S. O. Chan, C. H. Chew and B. H. Loo, J. Mater. Sci., 1996, 31, 1071.
27. H. Herrig and R. Hempelmann, Mater. Lett., 1996, 27, 287.
28. J. Fang, J. Wang, S. C. Ng and C. H. Chew, Nanostruct. Mater., 1997, 8, 499.
29. R. M. Rao, K. Rao, A. V. Prasada and S. Komameni, Mater. Lett., 1996, 1, 463.
30. L. Gao, H. Z. Wang, J. S. Hong, H. Miyamoto, K. Miyamoto, Y. Nishikawa and S. D. D. L. Torre, Nanostruct. Mater., 1999, 11, 43.
31. C. J. Brinker and C. W. Scherer, "Sol-Gel Science", Academic Press, San Diego, CA, 1990.
32. L. L. Hensch and J. K. West, Chem. Rev., 1990, 90, 33.
33. R. C. Mehrotra, A. Singh and U. M. Tripathi, Chem. Rev., 1991, 91, 1287.
34. E. D. Chandler, C. Roger and M. J. H. Smith, Chem. Rev., 1993, 93, 1205.
Kapoor et al.: Heterobimetallic mixed metal oxide (HMMO) nanoparticles and their applications

35. G. H. P. Liliane, *Polyhedron*, 1994, 13, 1185.
36. C. K. Narula in "Ceramic Precursor Technology and Its Applications", Marcel Dekker, New York, 1995.
37. R. C. Mehrotra and A. Singh, *Prog. Inorg. Chem.*, 1997, 239.
38. M. Bhagat, A. Singh and R. C. Mehrotra, *Main Group Met. Chem.*, 1997, 20, 89.
39. M. Bhagat, A. Singh and R. C. Mehrotra, *Synth. React. Inorg. Metal-Organic Chem.*, 1998, 28, 997.
40. R. C. Mehrotra, A. Singh, M. Bhagat and J. Godhwani, *J Sol.-Gel Sci. & Tech.*, 1998, 13, 45.
41. H. K. Sharma and P. N. Kapoor, *Indian J. Chem. .. Sect. A*, 2003, in press.
42. M. Sharma, A. K. Bhagi and P. N. Kapoor, Unpublished results, 2003.
43. D. R. Rolison and B. Dunn, *J. Mater. Chem.*, 2001, 11, 963.
44. F. Ribot, P. Toledano and C. Sanchez, *Chem. Mater.*, 1991, 3, 759.
45. S. S. Kistle, *Nature*, 1931, 127, 741; *J. Phys. Chem.*, 1934, 38, 52.
46. P. H. Tewari, A. J. Hunt and K. D. Loff tus, *Mater. Lett.*, 1985, 3, 363.
47. G. Pfaff, *Chem. Mater.*, 1994, 7, 58.
48. D. Demydov and K. Klabunde in "Symposium on Nanotechnology and its Potential Role in Homeland Security", Kansas State University, U.S.A., 2003, p. 22.
49. H. Shimooka, S. Kohiki, T. Kobayashi and M. Kuwabara, *J. Mater. Chem.*, 2000, 10, 1511.
50. S. Mathur, H. Shen, N. Lecerf, A. Kjekshus, H. Fjellvag and G. F. Goya, *Adv. Mater.*, 2002, 14, 1405.
51. P. N. Kapoor, D. Heroux, R. S. Mulukutla, V. Zaikovskii and K. J. Klabunde, *J. Mater. Chem.*, 2003, 13, 410.
52. S. Mathur, M. Veith, M. Haas, H. Shen, N. Lecerf and V. Huch, *J. Am. Ceram. Soc.*, 2001, 84, 1921.
53. A Y. Medvedev in "Mineralogical Magazine", 1996, 60, 347.
54. K. Hirota and R. C. Bradt in "Analytical Sciences", 1991, 7, 1275.
55. P. N Kapoor, S. Uma and K. J. Klabunde, Unpublished results, 2003.
56. Y. Teraoka and S. Kagawa in "Catalysis Surveys from Japan", 1998, 2, 155.
57. G. Fortunato, H. R. Oswald and A. Reller, *J. Mater. Chem.*, 2001, 11, 905.
58. M. S. D. Read, M. S. Islam, G. W. Watson and F. E. Hancock, *J. Mater. Chem.*, 2001, 11, 2597.
59. S. Rajuduraj, J. J. Carberry, B. Li and C. B. Alcock, *J. Catal.*, 1991, 131, 582.
60. R. Doshi, C. B. Alcock, N. Gunasekaran and J. J. Carbeny, *J. Catal.*, 1993, 140, 557.
61. N. Guiha me, S. D. Peter and M. Primet, *Appl. Catal.*, 1996, 10, 325.
62. H. Takasaki, S. Tanabe and T. Hanade, *J. Ceram. Soc. Jpn.*, 1995, 104, 309.
63. X. Y. Li, S. B. Li and G. X. Lie, *J. Mol. Catal.*, 1996, 31, 187.
64. P. K. Stoimenov, R. L. Klinger, G. L. Marchin and K. J. Klabunde, *Langmuir*, 2002, 18, 6679.
65. O. B. Koper, J. S. Klabunde, G. L. Marchin, K. J. Klabunde, P. Stoimenov and L. Bohra, *Curr. Microbio.*, 2002, 44, 49.