

## SYSTEMS BASED ON BaZrO<sub>3</sub> CONTAINING PRECIOUS METALS FOR CATALYTIC APPLICATIONS

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*Catalysts based on BaZrO<sub>3</sub> with precious metals inside the structure in a high oxidation state have been synthesised. They were found to be stable at high temperature and useful for the catalytic combustion in the high temperature range, thus solving a problem of the present technology and therefore completely avoiding the NO<sub>x</sub> formation. A USA patent and, recently, also an EU one have been granted.*

*The same catalysts have been used for the hydrogen production starting from gaseous or liquid hydrocarbons, air and water with an autothermal catalytic reactor characterized by a high efficiency because of the low CO<sub>2</sub> production. Also for this reactor an European patent has been granted.*

*All the above mentioned patents may be transferred to industries interested in developing them on an industrial scale*

### **Sistemi basati su BaZrO<sub>3</sub> contenente metalli preziosi per applicazioni catalitiche**

Sono stati sintetizzati catalizzatori a base di BaZrO<sub>3</sub> con metalli preziosi in struttura in un alto stato di ossidazione, stabili a temperature elevate ed utili nella combustione catalitica nell'intervallo più alto di temperatura, risolvendo quindi un problema della tecnologia attuale e permettendo così di evitare la formazione di NO<sub>x</sub>. È stato concesso un brevetto USA e di recente un brevetto UE.

Gli stessi catalizzatori sono stati usati per la produzione di idrogeno a partire da idrocarburi gassosi o liquidi, aria ed acqua con un reattore catalitico autotermico caratterizzato da un'alta efficienza perché produce poca CO<sub>2</sub>. Anche su questo reattore è stato concesso un brevetto UE.

Tutti i brevetti possono essere ceduti ad industrie che vogliono svilupparli su scala industriale.

### **Barium zirconate for applications in the area of superconductors**

The interest for barium zirconate received a strong boost in the 90s because it is the only suitable material for crucibles usable in melting processes of high critical temperature superconductors<sup>1</sup>.

BaZrO<sub>3</sub> is a material that has a very high melting temperature (about 2,600 °C) at which it arrives without phase transitions, a coefficient of thermal expansion lower than ZrO<sub>2</sub> which makes it more stable to thermal shock, and also is more economical than zirconium oxide because it does not require the presence of yttrium to be stabilized. For applications in the field of superconductors the powder is produced from BaCO<sub>3</sub> and ZrO<sub>2</sub> which are calcined together at a temperature of 1,200 °C, with repeated cycles, and intermediate grinding in a mill with ZrO<sub>2</sub> balls. After the third cycle grains smaller than one micrometer are obtained, a binder such as stearic acid is added, and the powder so obtained is compressed at 2,000 bar to obtain the desired shape of the crucible. A last calcination at 1,700 °C for 48 follows, from which a ceramic material is obtained with a density higher than the 98.5% of the theoretical value.

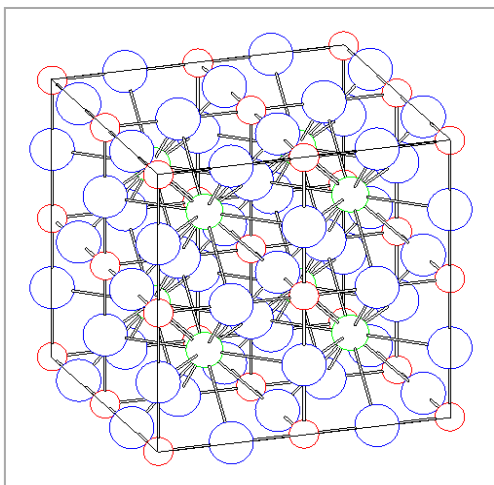
### **Barium zirconate for catalytic applications synthesized by the modified method of citrates**

The preparatory procedure described in the preceding paragraph, however expensive, is suitable, as mentioned above, for the production of ceramic materials to be used in the field of superconductors.

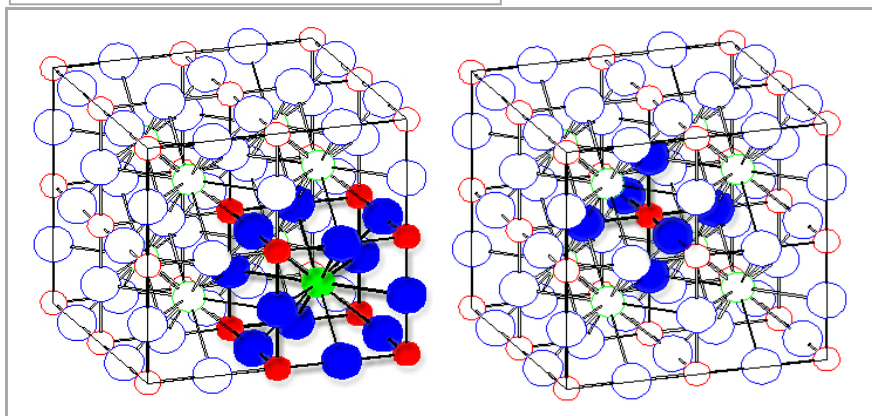
For applications in the area of catalysis, however, it is necessary to develop preparation methods leading to materials with a significant surface area.

For this purpose, a variant of the method of synthesis of the citrates was developed at the University of Aquila which has made it possible to obtain catalysts with perovskite structure containing Ba, much more stable than perovskites usually used based on La, and have precious metals inside the perovskite structure, in a high oxidation state. The presence of an unusually high oxidation state is due to the stoichiometry of the perovskite. Indeed in the perovskite formula  $ABO_3$ ,

(see Fig. 1) A is a cation with a great ionic radius. Therefore if A is a bivalent cation such as barium, cation B will be a tetravalent cation: Zr or in our case, also a precious metal cation, so as to balance oxygen charges. This does not occur for La which is trivalent<sup>2</sup> (Fig. 2)



*Fig. 1  
Ideal structure of a perovskite*



*Fig. 2  
Cations A (green) at cube centres and Cation B (red) at the centre of octahedra;  
blue spheres = oxygen anions*

The advantages related to the use of these systems are:

- high temperature stability, not present in catalysts currently used, which is required for industrial applications both for hydrogen production and for electric power generation<sup>2,3,4,5</sup>;
- indeed these systems, in addition to being useful for the production of hydrogen, may find an application in catalytic combustion, particularly in the high temperature range, in which stable catalysts are currently not available, and therefore they are suitable for the technology that allows the highest energy yields in electric power generation from natural gas (combined cycles)<sup>4,5</sup>;
- there is in this case the opportunity to eliminate  $NO_x$ , the only pollutants produced during combustion, in compliance with current regulations regarding environmental impact<sup>4</sup>.

Nevertheless, the method adopted for the synthesis has made it possible to obtain amounts of catalysts in the order of some hundreds of grams compared to what is usually carried out in university laboratories where normally amounts synthesized do not exceed a few grams. The “large scale” production has enabled measurements of catalytic activity and advanced physico-chemical characterization, in many laboratories: the Politecnico di Milano, the State University of Milan, Salerno, Roma-La Sapienza, Bologna, Parma, Genoa, Strasbourg, the Royal Institute in Stockholm, Eni San Donato Milanese and Eni Donegani di Novara.

As mentioned above, with the method developed systems are obtained unusually stable to temperature, with the precious metal present in the state that is more active even under drastic conditions, such as those often present in industrial conditions.

This stability may have an important impact not only in normal time-on-stream, but also during the regeneration of the deactivated and fouled catalysts, by controlled combustion of the carbon deposits: this is due to the stability of these systems at temperatures around 1,450 °C. For example in [2] it is shown that Pd is fit inside the

structure with a 4+ oxidation state, and that it is necessary to go over 1,450 °C to completely reduce Pd to the metallic state, while PdO supported on alumina is reduced to metallic Pd which is rather inactive already at 950 °C; on the other hand the systems containing Rh have an hysteresis concerning the oxidized-Rh metallic-Rh in the 1,200-1,000 °C range, therefore at very high temperatures: therefore the rhodium may be oxidized at 1,000 °C and fit back into the perovskite<sup>3</sup>.

It is noteworthy that the technology developed has shown that it is possible to directly stick the perovskite active phase on a support without carrying the usual coating pretreatment. In other words it is possible to stick stably and firmly the active phase both to ceramic supports such as alumina, zirconia, silicon carbide or cordierite or to a metallic support such as feccralloy.

In Fig. 3 in light grey is shown a feccralloy metallic foam, while in black it is the same foam covered with the perovskite catalyst, well stuck and resistant to thermal shocks.

A final advantage of the proposed method of preparation, which is not using nitrates, is that it allows the decomposition of the organic part in mild and better controlled conditions, without development of NO<sub>x</sub> and no risk of explosion, as can happen using some metals with oxidizing properties.

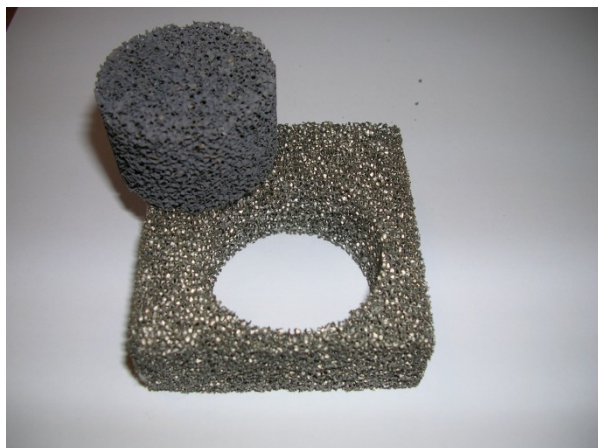


Fig. 3  
Feccralloy foam and the same covered with the perovskite catalyst

An European Patent has been granted<sup>6</sup> concerning an autothermal catalytic reactor with a flat temperature profile for hydrogen production with high conversion efficiency from light gaseous or liquid hydrocarbons air and water as reactants.

The reactor is characterized by:

- 1) a catalyst which favours the “direct “ hydrogen formation mechanism i.e. with a lower CO<sub>2</sub> formation in respect to the thermodynamic equilibrium (it is the Rh perovskite catalyst described above);
- 2) a specific structured support with a high porosity and tortuosity characterized by a high thermal conductivity;
- 3) a catalytic bed realized with a radial geometry rather than an axial one, so as to optimize the contact time;
- 4) a rapid start-up of the reactor which makes it suitable also for the distributed production.

The characteristics of this patent which concerns the reactor, are obtained using catalysts based on precious metals described above which obtained a USA patent and more recently also a European patent<sup>7</sup>. The Rh perovskite showed also an excellent performance in the methane steam reforming<sup>8</sup>.

This set of unique properties bodes well for industrial development.

All patents mentioned above can be sold to industries that want to develop them on an industrial scale.

### **Barium zirconate for catalytic applications synthesized by coprecipitation**

A coprecipitation method for the catalysts synthesis has now been developed, which bodes well for catalytic applications. The development of an alternative preparation method was suggested to obtain a good yield of catalysts with a minor use of resources particularly in the scale-up phase, and by the possibility of using reagents with a more controlled stoichiometry and reactivity.

This technology allows the manufacture of these systems, which are new, independently of the preparation method (see *claim* number 1 of [7]).

The new technology is based on a coprecipitation process at constant pH.

This new mode of synthesis of catalysts allows in the future to have a preparative method more easily developable on an industrial scale, more quickly and without the consumption of significant amounts of nitrogen cylinders for the controlled decomposition of the organic phase.

In the coprecipitation a solid containing as cations only barium, zirconium and the desired precious metal, such as rhodium or platinum must form. You can not use, for example sodium salts or potassium because you would find these two cations in the precipitate.

The only viable options are the processes of coprecipitation of hydroxides or carbonates, from which one can obtain the perovskite by subsequent calcination.

### Precipitation of hydroxides for the synthesis of a Ba-Zr-Rh perovskite

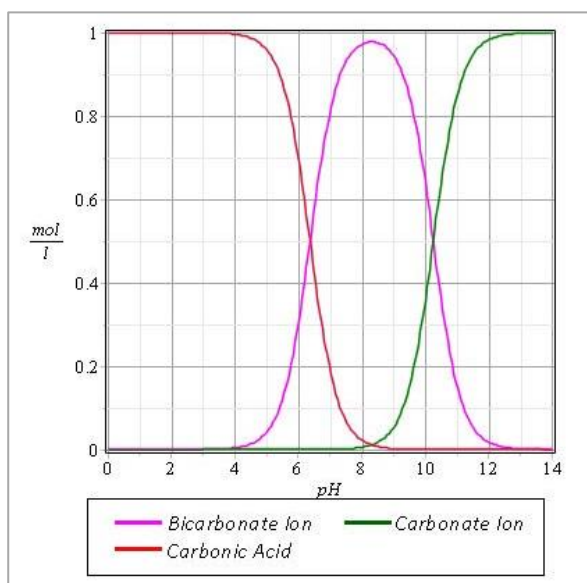
On the use of hydroxides some trials were carried out to try to obtain precipitates using only ammonia but, also working at different pH values, high losses of barium have always been found, as indeed was predictable, as the hydroxide of barium, also called water barite, is partially soluble.

The synthesis procedure involved the use of barium nitrate, rhodium nitrate hydrate and zirconyl nitrate performing a coprecipitation at constant pH and temperature of 70 °C, followed by a wash at the same temperature.

From the data collected it was found that the precipitation is far from quantitative. Also by increasing the pH value the amount of ammonia to be used grows exponentially up to values not commercially sustainable; the higher losses are those of barium, especially at pH below 7 and by increasing the pH a decrease in the loss of zirconium and an increase of the losses of rhodium were found. Finally, the Rietveld analysis of the samples calcined at 900 °C showed the formation at a pH below 7 of the tetragonal  $ZrO_2$  phase,  $BaRh_6O_{16}$  and  $Rh_2O_3$  while at higher pH a  $BaZrO_3$  phase forms with cell parameter 4.15-4.16 Å, indicating that rhodium has entered the perovskite phase.

### Precipitation of carbonates for the synthesis of a Ba-Zr-Rh perovskite

The only reasonable alternative to obtain a precipitate which contains all and only the desired cations is to precipitate carbonates.



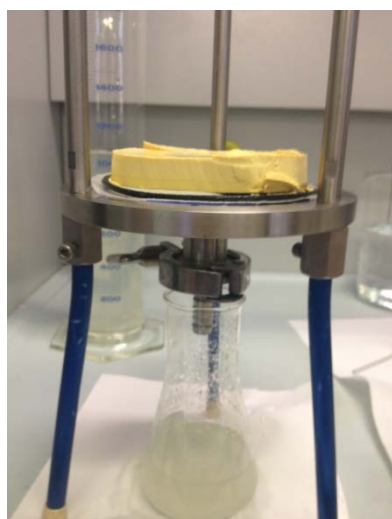
For this purpose, it must be remembered that in solution is not necessary the presence of bicarbonate ion but the carbonate which is present only at a pH greater than 12, a value impossible to achieve in the presence of ammonium carbonate (see Fig. 4).

Experimental tests carried out using ammonium carbonate also showed significant losses of zirconium. For these two reasons it is deduced that ammonium carbonate cannot be a good precipitating agent.

Finally, the zirconium-based reagent is normally available zirconyl nitrate,  $ZrO(NO_3)_2$ , salt that hardly allows for a quantitative precipitation. For this reason zirconium nitrate  $Zr(NO_3)_4$ , which is less commonly used, is employed.

Fig. 4

Concentration of bicarbonate ion, carbonate and carbonic acid vs. pH



The use of tetramethylammonium hydroxide, organic base comparable to caustic soda in strength, allowed to overcome all the difficulties mentioned above to obtain a quantitative precipitation of carbonates of barium, zirconium and rhodium. To this base was added a solution of ammonium bicarbonate to obtain a solution containing carbonate ions at very high pH and proceed to a coprecipitation, resulted to be quantitative, followed by a wash.

Fig. 5 shows the cake obtained after filtration in the pressure system, of which is evident the perfect homogeneity of the cake obtained to guarantee an excellent interspersions of the elements barium, zirconium and rhodium.

Fig. 5

Cake obtained after filtration under pressure

The sample after drying and calcination at 900 °C showed a perovskite phase with cell parameter 4.1652 (3) Å, index of a good insertion of the rhodium in the same phase. There were no other phases in which rhodium is present.

Also the catalyst with 1% platinum prepared by precipitation gave the x-ray diffractograms in line with the expected values. Both catalysts gave good performance in the catalytic combustion of methane.

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