

# Synthesis and Characterization of High-Temperature Stable Nanocomposite Catalysts

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## ABSTRACT

Unusually active and sinter-resistant nanocomposite materials were synthesized by combining the high reactivity of nanosized noble metal particles with the excellent high-temperature stability of hexa-aluminates through a simple one-step microemulsion-templated sol-gel synthesis. The novel nanocomposite catalysts were characterized by TEM, XRD, DTA and BET measurements after calcination at temperatures between 600°C and 1300°C, and were tested in the high-temperature partial oxidation of methane. The materials showed very high activity and selectivity along with excellent stability with respect to surface area, noble metal dispersion and catalytic activity over prolonged operation at reaction temperatures between 900 and 1100°C. To our knowledge, this is the first time that metal nanoparticles have been stabilized to such extreme high temperature conditions. We see these novel materials therefore not only as very promising candidates for high-temperature catalytic applications, but generally view this as a possible route to expand the parameter range for nanoparticle applications.

**Keywords:** nanocomposite materials, high-temperature stability, heterogeneous catalysis, hexaaluminates, methane oxidation

## 1 INTRODUCTION

The large surface areas of nanoscale particles as well as reports on novel chemical reactivity of particles with nanometer dimensions makes these materials highly interesting for heterogeneous catalysis. A particularly simple and well-controlled way to produce such materials is through micelle-templated syntheses, since the self-assembling properties of surfactants offer unique possibilities for the engineering of nanostructured materials [1-3]. Beyond allowing the template-directed synthesis of pore morphologies for nano- and mesoporous materials, the nanometer-sized droplets in reverse (water-in-oil) microemulsions also constitute a controlled environment for chemical reactions, such as sol-gel reactions, in which the micelles act as individual 'nano-reactors' [4-6].

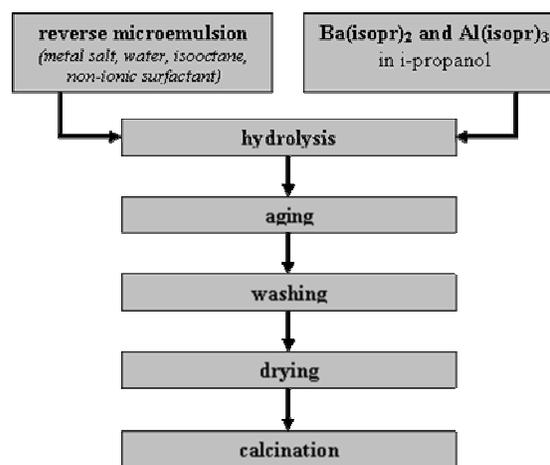
However, the use of such nanoscale materials is to-date restricted to low-to-moderate temperature conditions ( $T < 500^\circ\text{C}$ ), since the thermal stability of particles decreases rapidly with decreasing diameter. This imposes severe limitations for the application of these materials, particularly as catalysts for chemical processes. Here, the

conversion of hydrocarbons to hydrogen, synthesis gas and olefins at high-temperature, millisecond contact-time conditions has found much interest in recent years as a novel way for more efficient utilization of fossil and biomass-derived hydrocarbon resources [7-12]. While the high reactivity of noble metal nanoparticles would make such materials in principle ideally suited for millisecond contact-time catalysis, the extreme reaction temperatures ( $T = 800\text{--}1200^\circ\text{C}$ ) currently preclude such use.

In this contribution we report on the successful combination of the high reactivity of nanosized metal particles with the high-temperature stability of ceramics, resulting in unusually active and highly sinter-resistant nanocomposite materials for high-temperature catalytic applications.

## 2 SYNTHESIS

The synthesis of the nanocomposite materials is based on the simultaneous synthesis of a ceramic hexa-aluminate matrix and metal nanoparticles, using a microemulsion-templated sol-gel route. Figure 1 shows a schematic overview of the sequential synthesis steps: An aqueous noble metal salt solution, isooctane and one out of a number of different non-ionic surfactants are combined to yield a reverse (water-in-oil) microemulsion. Next, a solution of aluminum- and barium-isopropoxide in iso-propanol is added to the microemulsion, and the reaction mixture is aged for up to 72 hours under constant stirring at room temperature.



**Fig. 1:** Steps in the synthesis of noble metal barium-hexaaluminate catalysts.

Following these steps, the microemulsion is cooled to -20°C to achieve phase separation via thermally induced phase separation (TIPS). The oil phase is decanted and the product phase is washed several times to remove the remaining surfactant. Finally, the residue is dried in high vacuum and calcined in air at various temperatures between 600°C and 1300°C.

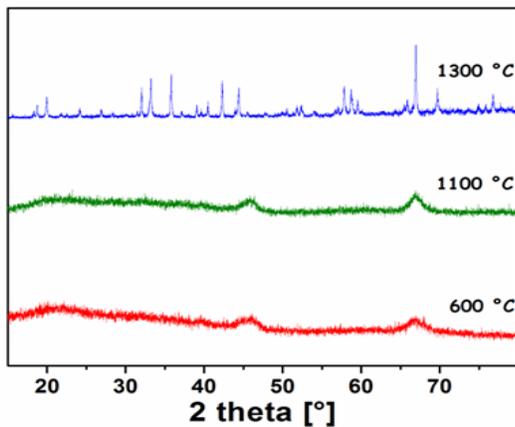
This procedure yields a fine powder which was used as synthesized for characterization as well as reactive tests.

### 3 CHARACTERIZATION

Pure barium hexaaluminate (BHA) samples as well as Pt-BHA nanocomposite materials which were synthesized as described above were characterized through XRD, DTA, BET and TEM measurements as described in the following.

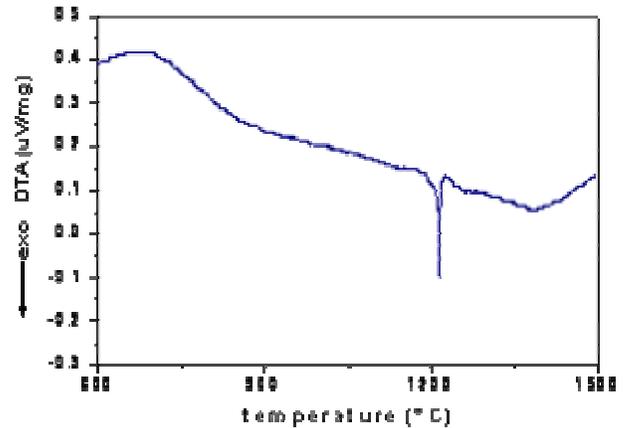
#### 3.1 Barium Hexaaluminate (BHA)

XRD measurements of a pure BHA sample synthesized according to the above describe route (without the addition of metal salt solutions to the microemulsion) reveal a largely amorphous ceramic structure at the lowest calcination temperatures of 600°C which persists even at temperatures as high as 1100°C (see figure 2). Only at calcination temperatures in excess of 1200°C the ordered structure of the high-temperature stable barium-hexaaluminate (BHA) structure becomes detectable.



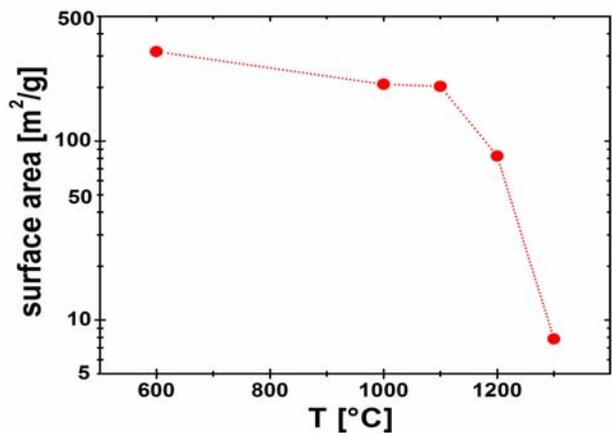
**Fig. 2:** X-ray diffractogram (XRD) of BHA synthesized in a reverse microemulsion and calcined at temperatures of 600°C, 1100°C and 1300°C.

This transition agrees well with DTA measurements of BHA samples shown in figure 3, which indicate a crystallization point of around 1200°C. As can be expected, the re-arrangement of atoms occurring upon crystallization of the hexaaluminate phase leads to a collapse of the large surface area.



**Fig. 3:** DTA scan of a pure BHA sample.

The structural stability of the ceramic matrix is furthermore reflected in the change of BET surface area of these materials with increasing temperature (see fig. 4): the materials as synthesized show very large surface areas in excess of 300 m<sup>2</sup>/g even after calcinations at 600°C. This large surface area is preserved fairly well up to calcinations temperatures as high as 1100°C, where surface areas of around 200 m<sup>2</sup>/g were measured. However, upon crossing the crystallization point for the ceramic host material (T>1200°C), the BET surface area collapses to values of 20 m<sup>2</sup>/g and less.

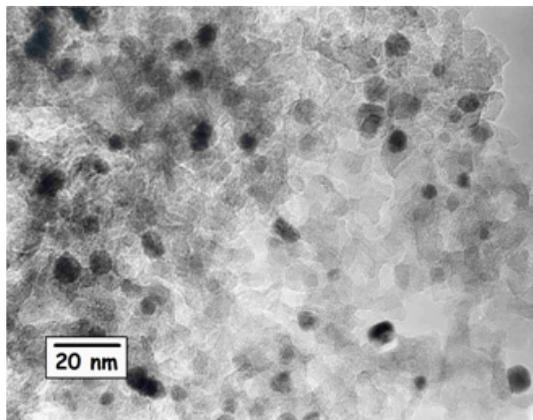


**Fig. 4** BET surface area vs calcinations temperature for a BHA sample after calcination for 5 hours in air at increasing temperatures.

#### 3.2 Pt Nanoparticles

The above described characteristics of the hexaaluminate matrix remained unchanged upon the addition of noble metal components to the synthesis. TEM investigations of the nanocomposite materials show that the

samples consist of loose agglomerates of nanoparticles with diameters of about 5 – 15 nm after calcination at 600°C (figure 5). Noble metal and hexaaluminate form separate but finely intermixed phases, i.e. the materials consist of metallic nanoparticles which are homogeneously dispersed in the matrix of the ceramic host material.

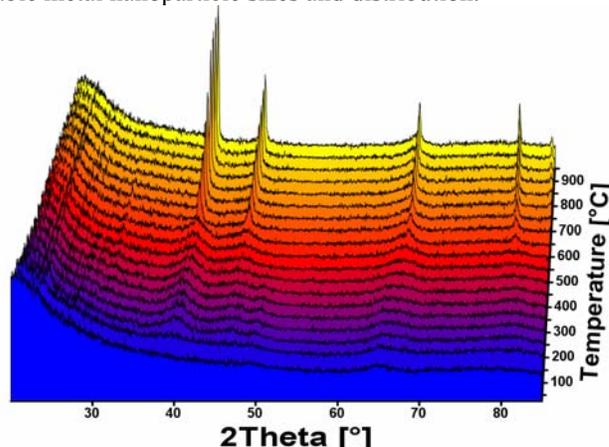


**Fig. 5:** TEM image of a Pt-BHA sample showing Pt nanoparticles (black) embedded in a matrix of BHA nanoparticles (grey). The sample shown had been calcined in air at 600°C for 5 h.

Both the particle distribution as well as the size of the Pt nanoparticles show very little change up to very high temperatures, indicating that through the reverse-microemulsion synthesis route, the metal nanoparticles appear to “inherit” some of the high-temperature stability of the ceramic host materials. TEM measurements show that the metal nanoparticles are stable up to temperatures around 1300°C (figure 6). However, both XRD and TEM also indicate that a small number of metal nanoparticles show an early sintering at lower temperatures which then dominates the XRD spectrum ( $T > 700^\circ\text{C}$ , figure 7).

Interestingly, the unusual stability of the noble metal nanoparticles is a highly sensitive function of the exact synthesis conditions. Several tests with post-impregnation

of pure BHA powders and even apparently minor modifications of the synthesis steps showed that only the above described simultaneous synthesis of metal and ceramic nanoparticles yields the reported high-temperature stable metal nanoparticle sizes and distribution.

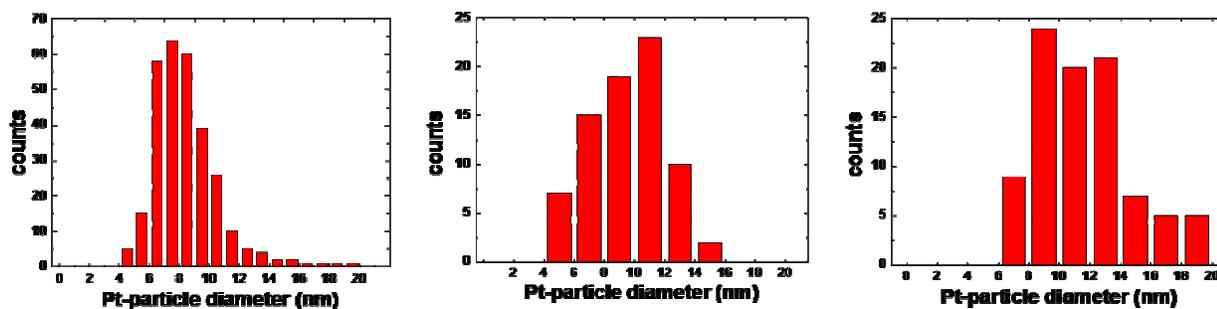


**Fig. 6:** High-temperature XRD scans of a nanocomposite Pt-BHA catalyst showing the onset of some sintering of Pt nanoparticles at about 700°C..

#### 4 CATALYTIC TESTS

The catalytic activity of the nanocomposite materials was tested in a simple tubular quartz-glass reactor using high-temperature catalytic partial oxidation of methane to synthesis gas as test reaction. We have previously reported on the drastic improvements in syngas selectivities as well as methane conversion over a Pt-BHA composite catalyst derived from a reverse microemulsion synthesis compared to a conventional Pt-coated alumina foam monolith [13].

Here, we highlight the extremely high reactivity of the obtained nanocomposite materials by showing results from an investigation in which we studied the influence of the platinum loading incorporated in the Pt-BHA catalyst. A series of syntheses was conducted in which the amount of platinum salt added during the material synthesis was



**Figure 7:** Particle statistics from TEM images of Pt-BHA catalysts after calcination at  $T = 600^\circ\text{C}$  (left),  $1100^\circ\text{C}$  (middle) and  $1300^\circ\text{C}$  (right). Very little sintering of the Pt particles is occurring with mean diameters increasing from 8.4 to 9.2 and 12.3 nm, respectively.

varied, yielding materials with a Pt weight loading between 0 and 30 wt%. TEM investigations showed that this increase in Pt-content in the material results in a higher platinum particle density while leaving particle sizes unchanged at about 5 to 10 nm. Also, the homogeneity of the distribution of the Pt-particles in the ceramic matrix remained unaffected.

## 5 SUMMARY

A novel type of catalyst material for high-temperature applications was synthesized via a reverse-microemulsion templated sol-gel synthesis in which noble metal and ceramic nanoparticles are synthesized simultaneously. The resulting material shows large, high-temperature stable surface areas and a very homogeneous distribution of noble metal nanoparticles dispersed in a ceramic host matrix.

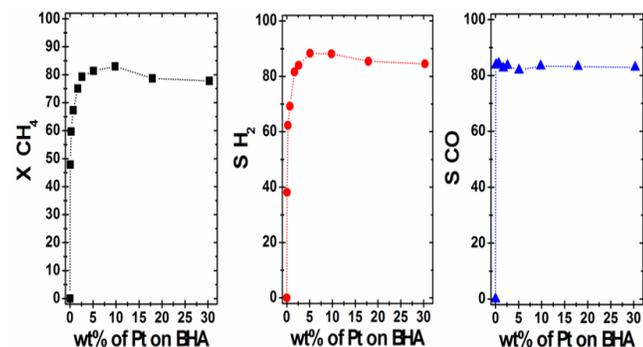
The ceramic phase is largely amorphous up to about 1200°C, while the metal nanoparticles show a rather narrow size distribution and very little sintering up to the same temperature range.

The catalysts were tested in the autothermal partial oxidation of methane to synthesis gas. They show excellent and selectivity at extremely low noble metal loadings (below 1 wt%). Most importantly, the materials appear high-temperature stable even after prolonged operation at reactive conditions

To our knowledge, this is the first time that metal nanoparticles were successfully stabilized to temperatures in excess of 800°C. We see these materials therefore not only as very promising candidates for high-temperature catalytic applications – such as hydrogen production by catalytic partial oxidation of hydrocarbon fuels - but generally view this as a possible route to expand the parameter range for nanoparticle applications.

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**Fig. 7:** Methane conversion, hydrogen selectivity and CO selectivity (from left to right) versus Pt weight loading of the Pt-BHA catalysts. Experimental conditions: CH<sub>4</sub>:O<sub>2</sub>:N<sub>2</sub> = 2:1:4, total inlet gas flow at standard conditions: 0.24 m<sup>3</sup>/s, adiabatic reactor operation.

The influence of the Pt amount in the Pt-BHA catalyst on the catalytic activity of the material is shown in figure 7. While pure BHA does not show any significant activity towards partial oxidation at any temperature studied in this investigation, even very small amounts of platinum already result in a noticeable catalytic activity and selectivity: A Pt-BHA catalyst with as little as 0.06 wt% Pt gave a methane conversion of 48% and a hydrogen selectivity of 38%. It seems remarkable that both oxygen conversion (not shown) and CO selectivity jump immediately upon Pt addition to their final values of 100% and ~82%, respectively.

Increasing the platinum content further, methane conversion and hydrogen selectivity increase very quickly to 60 % and 62%, respectively, at 0.24 wt% Pt, and reach a maximum of about 82% and 88%, respectively, at about 5 wt% Pt. Higher Pt-loadings do not lead to any significant changes in selectivity or conversion any more.

These results appear truly remarkable, since at the lowest Pt loadings and our typical reactor catalyst loading of 50 mg, the catalyst sample contains about 30 *micrograms* of platinum with significant conversion and yield at very high gas flow rates! This metal loading is several orders of magnitude below the loading that is necessary in conventional supported Pt catalysts and indicates the highly unusual catalytic activity of these nanocomposite materials.

Finally, it should be noted that even with the low weight loadings we did not see any catalyst deactivation over the course of our experiments (at least several hours of continuous operation), which confirms our previous findings that the high-temperature stability of these catalysts is in fact maintained at reaction conditions [13].