POTENTIALITY OF SUPERCRITICAL FLUIDS AS REACTIVE MEDIA TO SYNTHESIZE NANOSTRUCTURED MATERIALS.

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Supercritical fluids have shown an increasing interest as reactive media (tuneable properties from liquid to gas) to synthesize nanostructured materials by thermal decomposition of organometallic precursors at relatively low pressure and temperature. The particle formation process (nucleation and growth) is governed by high supersaturation in the supercritical fluid. So the adjustment of elaboration process parameters result in a precise control of particle shape and size (between 10 nm and 10 µm). In this paper, we present the synthesis of Co_2N, Cr_2N, Cr_2O_3 and TiO_2.

INTRODUCTION

Today one of the main challenges in materials science concerns the synthesis of nanomaterials. Actually nanomaterials exhibit new and interesting properties which are different of those of bulk materials. Consequently, numerous processes of nanomaterial synthesis are investigated [1-7] to reach a main goal: the control of the size, the morphology, the structure and the chemical composition of particles [8].

In this context, supercritical fluids show an increasing interest as reactive media (tuneable properties from liquid to gas) to synthesize nanostructured materials by thermal decomposition of metal precursors at relatively low pressure and temperature. More precisely the particle formation process (nucleation and growth) is governed by high supersaturation in supercritical fluids. So the adjustment of elaboration process parameters results in a precise control of particle shape and size (between 10 nm and 10 µm) [9].

The development of the process of nanostructured material elaboration in supercritical media (ICMCB) was performed with the synthesis of metal copper in supercritical CO_2/ethanol mixture. In this paper, we propose to discuss the influence of operating conditions on the nature, size, morphology and structure of other materials such as oxides and nitrides in supercritical NH_3/methanol mixture. For instance, we present the synthesis of Co_2N, a nitride with magnetic properties, Cr_2N, a material with interesting mechanical performances, Cr_2O_3, a catalyst for hydrogen storage [10] and TiO_2 with numerous industrial applications.

I – EXPERIMENTAL SECTION

Experimental set-up

The experimental set-up is a continuous process (Figure 1). It is composed of two pumps: one for pumping ammonia, the solvent, the other one for methanol, the cosolvent allowing to dissolve the metal precursors. In the first cell (the reactor) the thermal decomposition of precursor occurs. This chemical reaction allows the formation of fine particles which are carried out the reactor by the flow of supercritical fluid until the second cell (the collector). In the collector, the particles are stopped by a metallic filter perpendicularly placed into the fluid flow. At the end of the synthesis, the powder is collected in the second cell. The powder is dry and free of solvent.

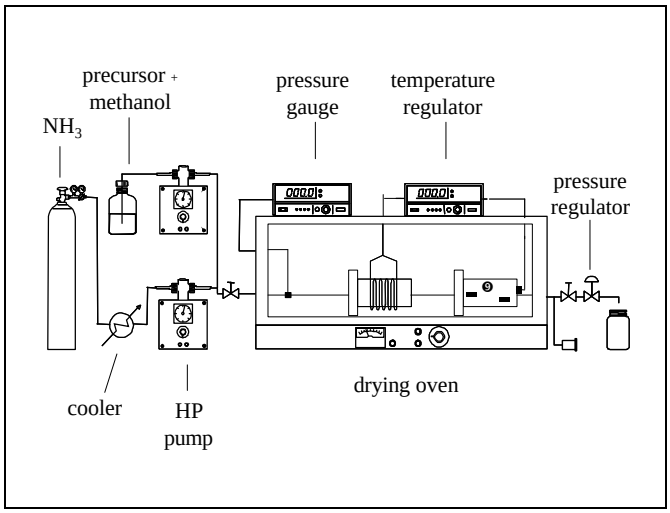

Figure 1: Experimental set-up for material synthesis in supercritical fluid

Experiments

The experimental conditions are summarized in Table 1. Ammonia was chosen as reaction media (T_C=132.4°C and P_C=11.29 MPa) because it exhibits a high reducing power and its critical temperature is lower than the one of metal precursor decomposition (above 200°C). Methanol is used as cosolvent in order to solubilize the metal precursor.

Three kinds of metal precursors, provided by Sigma-Aldrich or Strem (used without further purification) were tested. Experimental pressures were about 16MPa and temperatures between 230 and 260°C as a function of decomposition temperature of metal precursor.

Characterization

X-Ray Powder Diffraction, XPD (CuK α radiation), Electron diffraction - JEOL 2000FX microscope), Scanning Electron Microscopy, SEM - Jeol 840 microscope, Transmission Electron Microscopy, TEM - Jeol 2000 FX microscope. (Particle size determined by manual counting.)

II – RESULTS AND DISCUSSION

The results are laid out in Table 1.

The synthesis of materials in supercritical NH_3/methanol mixture from cobalt precursors led to cobalt nitride. This nitride was identified by XPD and electron diffraction (ASTM [Co_2N] n° 06-0647, [CoN] n° 16-0116) (Figure 2).

Table 1: Structure, chemical composition, morphology and size of crystallized domains of synthesized nanostructured materials

Test	Precursor	T (°C)	Structure	Chemical composition	Morphology	Size of crystallized domains
1	Cobalt hexafluoroacetylacetonate	260	Orthorhombic	Co_2N	Shapeless aggregates	60-120 nm
2	Chromium (III) hexafluoroacetylacetonate	260	Amorphous	Cr_2O_3+Cr_2N	Shapeless aggregates	***
3	Chromium (III) acetylacetonate	230	Amorphous	Cr_2O_3+Cr_2N	Shapeless aggregates	***
4	Titanium diisopropoxide bis(acetylacetonate)	230	Tetragonal	TiO_2	Shapeless aggregates	4-50 nm

As far as the morphology is concerned, Co_2N particles are organized in shapeless aggregates of few micrometers constituted of crystalline nanodomains of 60-120 nm.

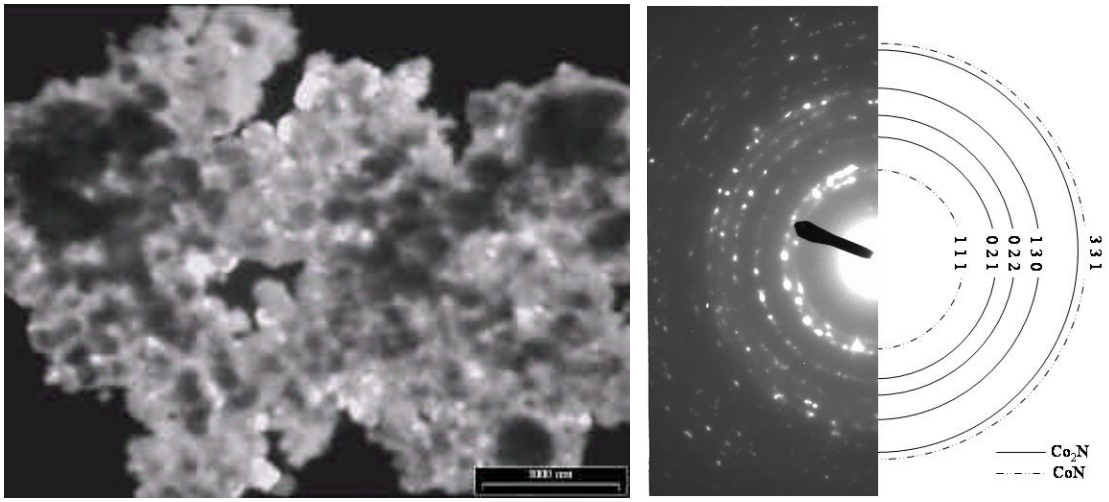

Figure 2: TEM picture and electron diffraction pattern (main diffractions) of Co_2N

The decomposition of chromium precursors in supercritical NH_3/methanol mixture induces the formation of a mixture Cr_2O_3/Cr_2N. The powder Cr_2O_3/Cr_2N was amorphous after the synthesis; a thermal treatment was performed and a crystallized material was

obtained. The obtained material was crystallized and characterized by XPD (Figure 3 – ASTM [Cr_2O_3] n°38-1479, [Cr_2N] n° 35-0803).
In addition, the same material, Cr_2O_3/Cr_2N, was synthesized with the two different chromium precursors: chromium (III) acetylacetonate and chromium (III) hexafluoroacetylacetonate.

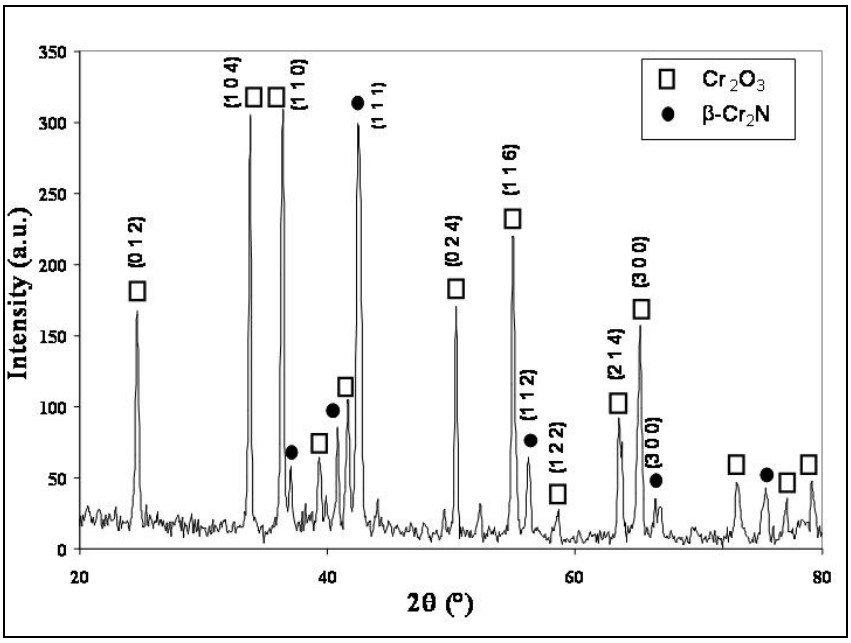

Figure 3: XPD pattern of Cr_2O_3/Cr_2N

Beyond the formation of a nitride and a mixture oxide/nitride, a third kind of material was obtained by decomposition of titanium precursor in the same experimental conditions (supercritical NH_3/methanol): an oxide, TiO_2.

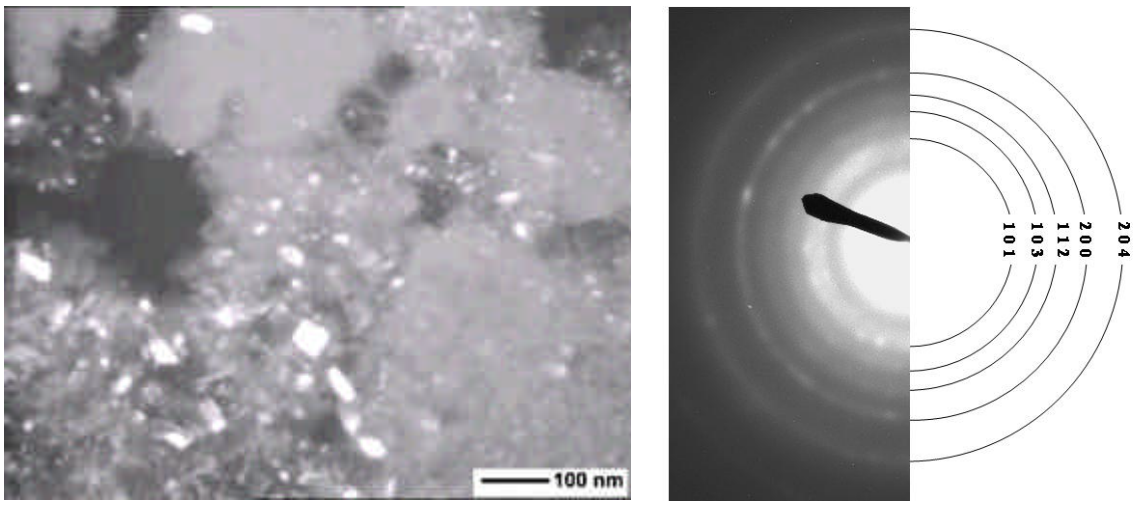

Figure 4: TEM picture and electron diffraction pattern of TiO_2

The titanium oxide is formed by aggregates of crystalline nanodomains of 4-50 nm (Figure 4). The identification was made thanks to ASTM information: [TiO_2] n° 21-1272.

Three different behaviours have been observed in regard with the metal precursor decomposition in supercritical NH_3/methanol: nitride formation (Co_2N), mixture oxide/nitride formation (Cr_2O_3/Cr_2N) and oxide formation (TiO_2). These results can be explained with the Ellingham diagram of oxide formation.

We can remark that the solvent (ammonia) and the cosolvent (methanol) are not previously dried; the synthesis always occurs in the presence of oxygen. On the one hand, metals for which the free energy of oxide formation is weak (Co) tend to only give metal nitrides because the ammonolysis reaction is favoured in regard with the metal oxidation reaction by the oxygen atoms dissolved in the reaction media. On the other hand, metals for which the free energy of oxide formation is high (Ti) lead to metal oxides. Between these two kind of metal family, there is a competition between ammonolysis and oxidation reaction for chromium which involves the formation of a mixture Cr_2O_3/Cr_2N.
The nitride formation being thermodynamically possible (Cr), the proportion of nitride could be increased by reducing the oxygen concentration in the reaction media.

CONCLUSION

Thanks to this study, the chemical composition of nanostructued materials elaborated in supercritical fluid can be controlled. Actually, the use of supercritical ammonia allows to elaborate at relatively low temperature nitrides if the free energy of oxide formation of the metal studied is not too high. Moreover, in the case of mixture oxide/nitride, it is possible to favour nitride synthesis by deleting oxygen in the reaction media.

Finally, the massive production of nanostructured materials is the major limiting factor of this process thus, a pilot facility of nanostructured materials (100 g/h of powder, 40 MPa, 300°C) is in progress in ICMCB.

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