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Solvothermal synthesis of microcrystallites of transition metal oxides

G. Demazeau[a,b,*], J.-M. Millet[c], C. Cros[a,b], A. Largeteau[a,b]

[a] *Institut de Chimie de la Matière Condensée de Bordeaux (I.C.M.C.B.-C.N.R.S.-UPR 9048), Avenue du Dr. Schweitzer, 33608 Pessac Cedex, France*

[b] *Interface Hautes Pressions, E.N.S.C.P.B., Avenue Pey Berland, 33402 Talence Cedex, France*

[c] *Institut de Recherche sur la Catalyse, Université Claude Bernard, 43 Bd du 11 Novembre 1918, 69622 Villeurbanne Cedex France*

Abstract

The development of solvothermal reactions is important in different basic and applied research areas. In order to illustrate the possibilities of such reactions, the preparation of microcrystallites which are well defined in size and morphology for different applications has been selected. The preparation of molybdenum oxides as a function of the chemical composition of the solvent and the experimental conditions (pressure, temperature, time...) will be described. © 1997 Elsevier Science S.A.

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1. Introduction

The preparation of microcrystallites well defined in size and morphology is an important challenge for various industrial applications including: finely divided pure oxides with high reactivity, precursors of fine ceramics, abrasive powders, optical or magnetic pigments, catalysts, etc.

In particular, the synthesis of new catalysts appears to be important, due to their potential use in many domains: synthesis of organic chemicals, petrochemistry, environmental chemistry, etc. Solvothermal reactions are a powerful route for the preparation of such microcrystallites [1]. Different ways have recently been explored either for developing new catalysts [2,3] or for improving the synthesis of new oxides [4] which can be used as an interphase in composite materials.

Solvothermal reactions consist of chemical reactions in a solvent in supercritical conditions or near these conditions [5]. Three different routes are possible:

1. the solvothermal precipitation of the solid phase when the reactants are soluble in the solvent;
2. the solvothermal decomposition of the precursors insoluble in the solvent;
3. the solvothermal recrystallisation of the finely divided amorphous starting material with the same composition as the final microcrystallites.

Molybdenum oxides have been selected to illustrate. The composition of the solvent as well as the pressure and temperature values are used as variables.

* Corresponding author.

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Table 1
Composition of the resulting microcrystallites vs. the chemical composition of the solvent

Composition of solvent		P (MPa)	T (°C)	Resulting phase from XRD analysis
% H_2O	% C_2H_5-OH			
100	0	30	500	No single phase
20	80	50	500	MoO_2
0	100	30	500	MoO_2

2. Preparation of molybdenum oxides through solvothermal reactions

$(NH_4)_2MoO_4$ containing Mo(VI) was selected as the starting material, the ammonium salts being soluble in aqueous solvents.

Previous work [1] has pointed out that ethanol is characterized by reducing properties as solvent in solvothermal conditions. For example, using goethite FeOOH as the starting material in a mixture of C_2H_5-OH and H_2O (50/50), the formation of Fe_3O_4 microcrystallites is observed through solvothermal reaction.

Table 2
Experimental conditions of the solvothermal synthesis of MoO_2 microcrytallites at increasing pressures

T (°C)	P (MPa)	Volume of liquid (cm^3)	Resulting phase from XRD analysis
400	12.5	7.4	MoO_2
400	13	11	MoO_2
400	17	14.8	MoO_2
400	28.5	18.5	MoO_2
400	43.5	22.2	MoO_2
400	97	25.9	MoO_2
400	123	29.6	MoO_2
400	203	33.3	MoO_2

Consequently, the solvent was selected with a variable composition between pure H_2O and pure C_2H_5-OH in order to define the optimum composition for the reduction of Mo(VI) to Mo(IV) with the formation of MoO_2.

In a second step, the size and the morphology of the resulting MoO_2 microcrystallites have been evaluated vs. different parameters:

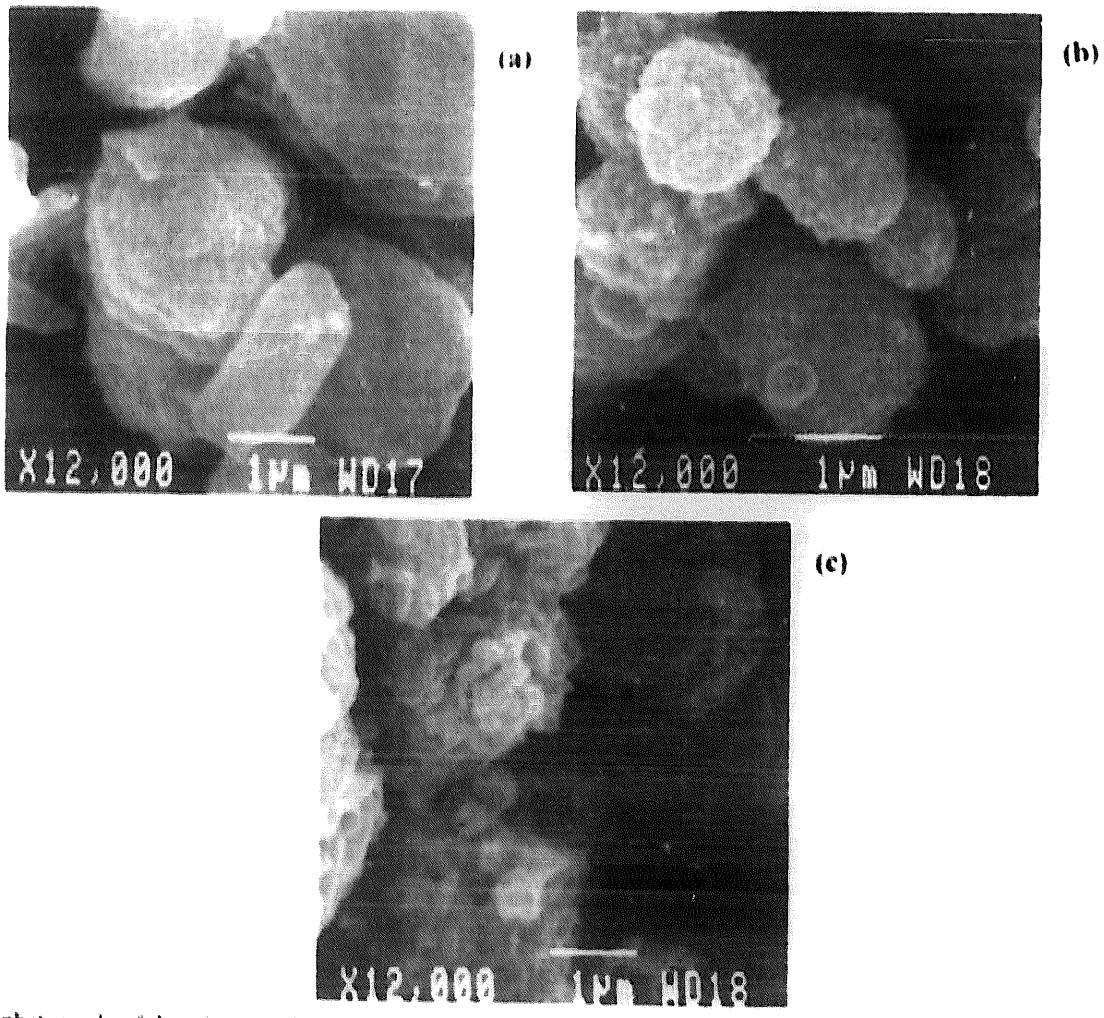

Fig. 1. SEM photographs of the microcrystallities for different conditions: (a) 400°C, 13 MPa; (b) 400°C, 29 MPa; (c) 400°C, 123 MPa.

Table 3
Experimental conditions of solvothermal synthesis of MoO_2 microcrystallites at increasing temperatures

T (°C)	P (MPa)	Volume of liquid (cm^3)	Resulting phase from XRD analysis
300	95	37	No single phase
350	95	29.6	MoO_2
400	95	25.9	MoO_2
500	95	18.5	MoO_2
550	95	18.5	MoO_2
600	95	18.5	MoO_2

1. composition of the solvent;
2. pressure;
3. temperature.

2.1. Solvothermal synthesis of MoO_2 microcrystallites as a function of the composition of the solvent (H_2O / C_2H_5-OH)

Several experiments have been carried out using the same precursor $(NH_4)_2MoO_4$, with a constant value of P and T, but with varying compositions of the solvent. The results reported in Table 1 show that MoO_2 microcrystallites are obtained with a solvent composition between 0% and 100% of water with 100% and 0% of ethanol.

2.2. Morphology and size of MoO_2 microcrystallites as a function of pressure

In order to study the influence of increasing pressures on the morphology and size of the MoO_2 microcrystallites, a series of experiments has been carried out using the same precursor, a composition of the solvent of 50% H_2O + 50% C_2H_5-OH and a temperature of 400°C for a reaction time of 10 min (Table 2).

Fig. 1 shows the SEM photographs of the resulting microcrystallites. The morphology of the MoO_2 microcrystallites as a function of pressure is always of spherical-type, but varying size and surface (Table 2).

2.3. Morphology and size of MoO_2 microcrystallites as a function of the temperature of preparation

Using $(NH_4)_2MoO_4$ as the starting material, a

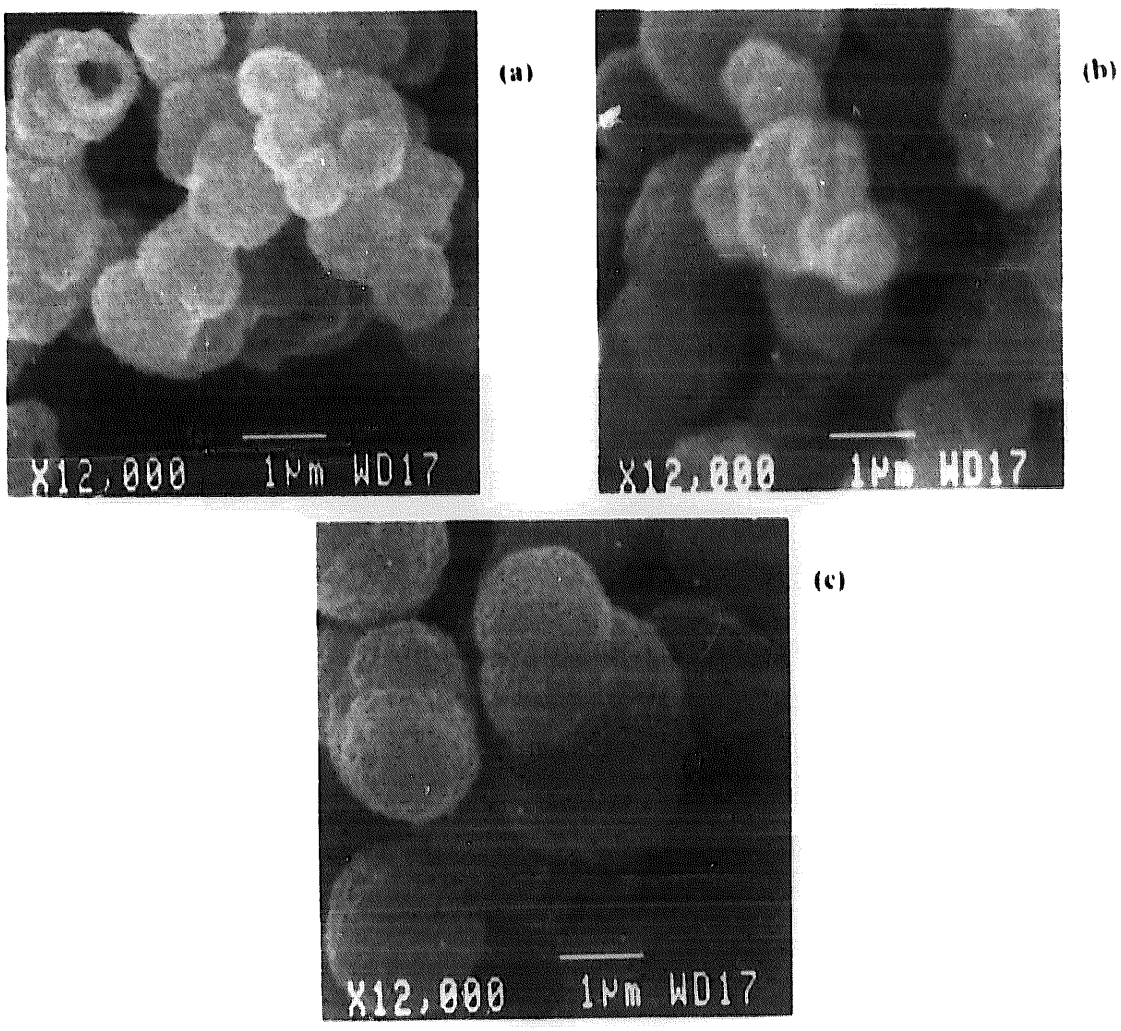

Fig. 2. SEM photographs of the microcrystallites for different conditions: (a) 400°C, 95 MPa; (b) 500°C, 95 MPa; (c) 550°C, 95 MPa.

pressure value of 95 MPa and a solvent composition 50% H_2O + 50% C_2H_5-OH, several solvothermal reactions have been carried out at different temperatures for a reaction time of 10 min (Table 3). Fig. 2 illustrates the evolution of size and morphology of MoO_2 microcrystallites in such experimental conditions in the temperature domain $300 \leq T \leq 600$°C.

3. Conclusions

This preliminary study underlines the possibilities of the solvothermal reactions for the preparation of MoO_2 microcrystallites devoted mainly to catalytic applications and opens the way to the synthesis of other reduced molybdenum based oxides. The comparison of the catalytic properties in oxidation and oxidative dehydrogenation reactions of MoO_2 prepared using the solvothermal reaction and a conventional sol/gel method has been undertaken.

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