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Synthesis of solid materials in molten nitrates

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Contents

Abstract

Chemical methods of synthesis of materials play a crucial role in the design and discovery of new materials, and also provide better and less cumbersome methods for preparing known materials. In this paper, the synthesis of inorganic compounds in molten nitrates is discussed. This method can be envisaged in some cases as a soft chemistry route for the preparation of solids. The reaction mechanisms of transition-metal salts and their mixtures in molten nitrates are given. Then, the preparation of dispersed simple oxides, multicomponent systems, layered intercalation hosts and supported catalysts are described. In the field of catalysis, the prepara-

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tion of solids with controlled textural properties is an important task. Several examples of this molten salt synthesis approach are given with the objective of optimising textural properties for catalytic applications. Management of the reaction can be obtained by modifications of the molten bath by using some dopant such as a nitrite or a carbonate. Examples illustrate the role of this dopant on the crystallisation rate and/or the reaction mechanism.

Keywords: Catalysis; Hydrotreatment; Molten salts; Nitrates; Rare earth oxides; Supports; Synthesis; Transition metal oxides

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1. Introduction

Molten salts as reaction media provide an alternative to aqueous chemistry by offering the possibility to change the solubility and/or the reactivity of the reactants, and to increase the reaction temperature [1]. Reactive fluxes have traditionally been used for the preparation of solids, recrystallization and growth. So far, attention in this field has been largely focused on the alkali and alkaline-earth halides [2] and polychalcogenides [3,4]. To grow anisotropic crystals, KCl–NaCl [5] and K_2SO_4–Na_2SO_4 [6] fluxes have been used, as well as molybdates [7] and tungstates [8]. Alkali carbonate and alkali hydroxide fluxes have also been used for the preparation of various oxides [9]. The oxosalts display a chemistry of great complexity and include several melts of industrial importance, i.e. sulphates, carbonates, borates and silicates. In molten media, reactions are usually controlled by chemical equilibria and proceed much faster than diffusion-controlled solid-state reactions. These oxosalts offer a wide range of reaction temperatures (see Table 1) and a great variety of possible chemical reactions, including those of complexation, oxidation–reduction, and acid–base type reactions.

Acid–base type reactions occurring in molten oxosalts are classified as Lux–Flood (L–F) acid–base reactions [10,11], oxide donors and acceptors being defined as L–F bases and acids, respectively, and the reaction is understood as follows:

$$\text{Oxoacid} + O^{2-} = \text{Oxobase} \qquad (1)$$

The basicity of the melt is usually expressed by $pO^{2-} = -\log m(O^{2-})$, where $m(O^{2-})$ corresponds to the concentration of O^{2-} ions. Depending on the reactant and basicity of the oxosalt, precipitation of an oxide or formation of an oxoanion can occur in the molten bath. For example, the reaction of silicon tetrachloride with

Table 1
Melting points of some oxosalt mixtures (m.p.: melting point)

Molten salt	$NaNO_3$–KNO_3	Li_2CO_3–Na_2CO_3	Li_2SO_4–K_2SO_4	$LiBO_2$–KBO_2	Na_2SiO_3–K_2SiO_3
Composition (mole%)	50–50	50–50	71.6–28.4	56–44	18–82
M.p. (K)	501	773	808	855	1026

an oxosalt melt at moderate pO^{2-}leads to precipitation of silica:

$$SiCl_4+2O^{2-}\rightarrow SiO_2+4Cl^-, \tag{2}$$

whereas if the melt basicity is further increased (low pO^{2-}), redissolution of SiO_2 may occur, caused by formation of metasilicate:

$$SiO_2+O^{2-}\rightarrow SiO_3^{2-}. \tag{3}$$

Then, depending on the nature of the molten salt, different species can be obtained and the nature of the products can be controlled.

2. The chemistry of molten nitrates

Alkali metal nitrates have been selected for many investigations because of their low cost, and above all, their conveniently low melting points [12–14] (see Table 2). Thermal decomposition of the nitrates occurs with measurable rates only above 823 K, which provides a large temperature range for studying the reactivity.

Molten nitrates can be envisaged as basic and oxidising media towards the majority of chemical compounds. These properties, respectively, depend on the ability of the nitrate anion to be an oxygen anion, O^{2-} donor, or an oxygen atom donor. The overall reactions of molten nitrates with all the main types of inorganic compounds are known but data on the nature of reacting species and equilibria between them remain contradictory [15–18]. The following equations can be proposed to describe L–F interaction of molten nitrates with appropriate ionic or neutral oxoacids:

$$NO_3^-+\text{Acid}\rightarrow NO_2^++\text{Acid.}O^{2-}, \tag{4}$$

$$NO_2^++NO_3^-\rightarrow 2NO_2+\tfrac{1}{2}O_2. \tag{5}$$

Reactions of the main classes of inorganic compounds were studied extensively by Kerridge et al. [19,20], including reactions of transition metals, lanthanides, and main group elements such as Bi and P. Generally, the products are oxospecies such as soluble oxoanions or oxide precipitates, as shown in Table 3.

For example, zirconium oxide is obtained from zirconium(IV) salts according to the following equation:

$$ZrOCl_2.8H_2O+2NO_3^-\rightarrow ZrO_2+2NO_2+2Cl^-+\tfrac{1}{2}O_2+8H_2O. \tag{6}$$

Soluble oxoanions can be produced from molybdenum oxide which undergoes

Table 2
Melting points of pure alkali metal nitrates and their low-melting mixtures

Molten salt	$LiNO_3$	$NaNO_3$	KNO_3	$LiNO_3$–KNO_3	$LiNO_3$–$NaNO_3$–KNO_3
Composition (mole%)	–	–	–	43–57	30–17–53
M.p. (K)	527	583	610	405	393

Table 3
Examples of products obtained by the reaction of precursor salts in molten nitrates

Oxides	CaO [21], MgO [22], ZnO [23], HgO [24]	Al_2O_3, La_2O_3 [25], CeO_2 [25]	TiO_2, ZrO_2 [26]	Bi_2O_3 [34]		MnO_2	Fe_2O_3 [27], NiO [23], RuO_2, CuO [35]
Oxo-anions			TiO_3^{2-} [28], SiO_3^{2-} [29]	PO_4^{3-} [30], VO_4^{3-} [31], NbO_3^-	SO_4^{2-} [22], MoO_4^{2-}, WO_4^{2-}	$Mn_2O_5^{2-}$ [32], IO_6^{5-} [33]	FeO_4^{2-} [27], RuO_4^{2-}

stepwise transformations (Eqs. (3)–(6)), leading to alkali metal molybdates A_2MoO_4 (A = K, Na):

$$3MoO_3 + 2NO_3^- \rightarrow Mo_3O_{10}^{2-} + 2NO_2 + \tfrac{1}{2}O_2, \quad (7)$$

$$2Mo_3O_{10}^{2-} + 2NO_3^- \rightarrow 3Mo_2O_7^{2-} + 2NO_2 + \tfrac{1}{2}O_2, \quad (8)$$

$$Mo_2O_7^{2-} + 2NO_3^- \rightarrow 2MoO_4^{2-} + 2NO_2 + \tfrac{1}{2}O_2. \quad (9)$$

Usually these mechanisms are deduced from thermogravimetric analysis of the reaction or mass spectra of the evolved gases during the reaction. Recently, we tried to characterise the nature of the products with extended X-ray absorption fine structure spectroscopy (EXAFS). This allowed us to confirm the structure of the intermediate species and to determine quantitatively their relative proportions at various reaction temperatures [36].

Doping of the melts with alkali metal oxides, peroxides [37], or other strong bases and oxidants may change the reactivity or (and) stabilise some unusual oxidation numbers [38]. Thus, the nature of the products can be managed by slight modifications of the melt.

Molten nitrates can also be used as a medium for host–guest reactions. A cation-exchange reaction was performed by Miyake et al. [39] in pure nitrate (MNO_3 with M = Li, Na, Rb, Ag) just above the melting point. In a $K_2W_4O_{13}$ host structure, alkali metal ions are located in the interlayer space. Topotactical exchange of this cation was performed in the nitrate melt providing new solids such as $Ag_{1.5}K_{0.5}W_4O_{13}$, $LiKW_4O_{13}$.

Contrasting with the numerous studies on molten nitrate chemistry, few studies have been devoted to the preparation and characterisation of solids issuing from these melts. The purpose of the present review is to demonstrate the preparative possibilities of molten nitrates for the synthesis of solids.

3. Synthesis of solids in molten nitrates

3.1. Experimental technique

Molten nitrate synthesis is simple and rather fast. The preparation is usually performed in a Pyrex glass reactor in air or under an inert atmosphere [19]. Although molten nitrate does cause some corrosion of the glass in the long term (see reaction Eq. (3)), in practice the amount of silicate formed is so small that its presence in the solid products is negligible. The precursor salt(s) is (are) mixed with a large excess of the nitrate salt (usually in our experiments a 10–20 fold molar excess). The most often used melts were the equimolar $NaNO_3$–KNO_3 mixture (mp = 501 K), or individual alkali metal nitrates. The mixture is pretreated at 423 K to eliminate water from the precursor salt(s) in order to avoid violent gas evolution upon melting. The reaction itself is carried out above the melting point. After cooling down, the solidified melt is thoroughly washed with distilled water to separate the (necessarily water-insoluble) solid product from the soluble salts. Then the product is dried in air at 393 K. Details on the nature of the precursor salts and reaction conditions are given in the references. For catalytic applications, the dried product is usually calcined in air at 683–773 K.

3.2. Preparation of simple oxides

As mentioned above, several metal oxides can be precipitated from molten salts (MS). Since these oxides can be easily prepared by other more simple methods, one reason for using molten salt technique is, for instance, to obtain unusual morphologies, not available otherwise. Both low melting temperatures of molten nitrates, as compared with other ionic fluxes, and their instability in the long term, make them inappropriate for performing crystal growth. By contrast, highly dispersed powders can easily be obtained from the molten nitrates. Simple oxides such as zirconia, alumina, ceria or titania have been synthesised by this way and the structures and textures of the products characterised.

3.2.1. Zirconium oxide

MS preparation of this oxide is the most extensively studied. Zirconia attracts considerable interest as a support material in a variety of catalyst systems [40]. However, the performance of such a new system depends to a large part on the texture and stability of the support, which for zirconia is always lower than for commercial alumina supports. Another problem is related to the polymorphism of this oxide, which can exist in the tetragonal or monoclinic forms. The preparation of dispersed tetragonal zirconia with high and thermally stable surface area is a difficult task; considerable experimental effort has been devoted to its accomplishment [41]. Compared to other methods, MS preparation showed promising results.

The formation of ZrO_2 in the reaction of Zr(IV) sulphate with a molten nitrate was first reported by Kerridge and Cancela Ray [24] and later in Ref. [42]. Jebrouni et al. [43] demonstrated that the reaction of hydrated $ZrOCl_2$ with molten KNO_3, $NaNO_3$ or their mixtures can be used for the preparation of ZrO_2 for ceramics or catalytic supports. Zirconia obtained at 450 °C was highly divided and pure, whereas the solids obtained at 260–360 °C were amorphous and contained high amounts of residual nitrate.

Several studies were devoted to the influence of the MS reaction conditions on the properties of zirconia obtained. The nature of the cation of the alkali metal nitrate has a strong influence on the properties of the oxide [44], affecting the specific surface areas, as well as pore size distributions (see Fig. 1).

This effect has been attributed to the solvating effect of the ionic melt, highly divided particles of zirconia being more or less stabilised depending on the nature of the alkali metal cation.

It has been shown by transmission and scanning electron microscopies that the oxide obtained from molten nitrates has nearly spherical morphology, very different from that of aqueous precipitates, which are rough and irregular. It may be one of

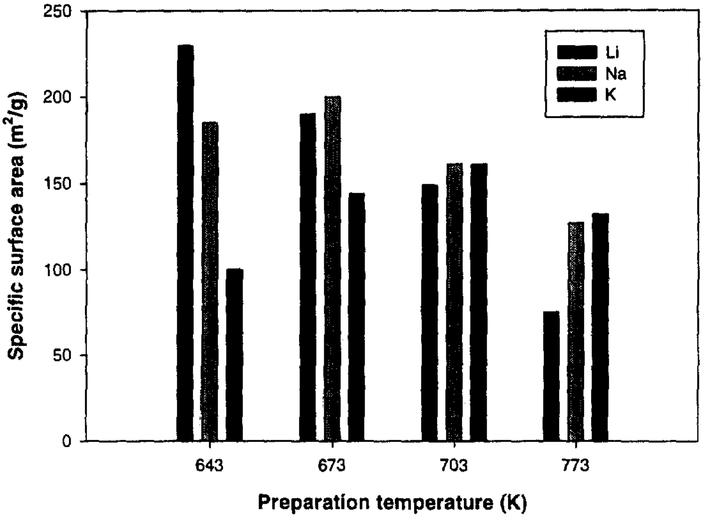

Fig. 1. Specific surface areas of zirconia synthesised in different alkali metal nitrates versus preparation temperature (adapted from Ref. [44]).

the reasons for its higher stability toward calcination. This parameter is important for catalytic applications.

Among other nitrates, $LiNO_3$ showed the highest reactivity, but the content of alkali metal cation impurity was also the highest. This is probably due to its small size and facility to enter into different solid lattices. This concerns not only zirconia but also any oxide systems: $LiNO_3$ being applied alone or in the mixtures with other nitrates is difficult to eliminate from the solid after the reaction.

The influence of acidity/basicity of nitrate melt on the phase composition and the crystallite size of zirconia powders prepared in the $NaNO_3$–KNO_3 mixture was investigated by Du et al. [45]. Adding L–F bases ($NaNO_2$, Na_2O_2, Na_2CO_3) to the system, the authors found the expected lowering of reaction temperature due to the increase of basicity. They also noticed variations in phase composition of the solid product with the concentration of the bases contained in the melt. A pure tetragonal phase could be produced above a certain value of base content. The crystallite size was found to decrease in the order $Na_2O_2 > Na_2CO_3 > NaNO_2$.

In other studies [46,47], the effects of the starting materials of α-$Zr(SO_4)_2$ and β-$Zr(SO_4)_2$, the different nitrate and nitrite melts, and the reaction conditions on the properties of ZrO_2 were investigated. Fine ZrO_2 powders (XRD size 3.8–16 nm) with a weak agglomeration of particles could be produced.

It seems however that if prepared from sulphate precursors, zirconia often retains considerable amounts of residual sulphate, which may strongly modify its properties (for catalytic applications where pure zirconia is needed, an impurity content above 0.2–0.3% is not acceptable). To remove this sulphate, either the reaction temperature had to be increased, or some bases had to be added, the first way leading to a decrease of surface area and the second to the incorporation of alkali metal cations.

The works cited above demonstrate the capability of MS synthesis for preparing zirconia powders with controlled texture. If the parameter to optimise is the specific surface area (a high purity of the solid being preserved), the best preparation technique is apparently the reaction of oxychloride precursor in the $NaNO_3$–KNO_3 melt at ca. 500 °C for at least 2 h. These preparative conditions give an oxide powder with a specific surface area of about 120 $m^2\ g^{-1}$ and a total impurity level of less than 0.1% (mostly Na) [44].

3.2.2. *Aluminium oxide*

Reactions of anhydrous aluminium salts with nitrate melts were first studied by Kerridge and Shakir [48]. The formation of α-alumina was noted and the reaction stoichiometry established, but no further characterisation of the oxide was made.

Aluminium oxide has been prepared by Du and Inman [49] from the reactions of anhydrous $Al_2(SO_4)_3$ or $AlCl_3$ with molten nitrates, nitrites, or nitrates with the admixture of L–F bases. On the basis of a thermogravimetric study, the following reactions of $Al_2(SO_4)_3$ in the nitrate and nitrite were proposed:

$$Al_2(SO_4)_3 + 6NO_2^- \rightarrow Al_2O_3 + 3NO_2 + 3NO + 3SO_4^{2-}, \qquad (10)$$

$$Al_2(SO_4)_3 + 6NO_3^- \rightarrow Al_2O_3 + 6NO_2 + \tfrac{3}{2}O_2 + 3SO_4^{2-}. \qquad (11)$$

In these reactions, poorly crystalline alumina has been produced with the X-ray diffraction (XRD) crystallite sizes between 2 and 5 nm, depending on the composition of the melt and precursor used (sulphate gave somewhat larger crystallite size than chloride).

The nature of the starting compounds is of primary importance in the case of aluminium. If highly reactive anhydrous salts were taken, the reaction occurred at very low temperatures, to some extent already upon mixing, and α-alumina was formed. By contrast, when some hydrated Al(III) salts were used, the reactivity was much lower and the properties of the product were quite different. We found that the solid obtained from the hydrated Al(III) chloride or nitrate at 450–550 °C in molten $NaNO_3$, KNO_3 or their mixture, was virtually amorphous. On contact with washing water it could easily be hydrated, forming crystalline $Al(OH)_3$ as Bayerite. Since the washing step leads to the chemical transformation of the product, the MS preparation for alumina from hydrated precursors seems rather useless. Moreover, though well-dispersed aluminium oxide could be prepared from molten nitrates, more simple precipitation routes give at least as good textural parameters as the MS technique.

3.2.3. *Lanthanum oxide*

Since La (III) is a weak L–F acid, the reaction of $LaCl_3$ occurs at high temperatures (above 450 °C). It is difficult to accomplish because the intermediate product LaOCl is poorly reactive and insoluble. Though, if the reaction is pushed to completion by the addition of bases or long exposure at 550–600 °C, the corresponding oxide La_2O_3 can be observed in the solidified melts. Washing of the reaction product with water always leads to crystalline $La(OH)_3$ as in the case of alumina. However, the reaction of $LaCl_3$ seems to be of some interest since pure LaOCl can be obtained at 450–500 °C (Fig. 2).

Using the MS preparation, this compound possesses highly oriented sheet-like morphology, as can be seen from the scanning electron microscopy images (see Fig. 3). The oxychloride obtained by this method can be used as an intercalation host [50], or as a reactive precursor for further solid preparations.

3.2.4. Cerium oxide

Reactions of Ce(III) and Ce(IV) salts (chloride, sulphate) have been studied in molten $NaNO_3$–KNO_3. CeO_2 was precipitated, having specific surface areas in the range of 10–30 $m^2 g^{-1}$ [51]. When Na_2O_2 was added to the melt, the reaction temperature decreased and an almost tenfold increase of the specific surface areas of the ceria products was observed. The presence of Na_2O_2 stabilised nanosize crystallites of ceria. Such textural properties may have some interest for catalytic applications.

An interesting observation made in Ref. [51] concerns the evolution of the oxidation state of cerium. The starting salt Ce(IV) sulphate was transformed at 370 °C to $NaCe(SO_4)_2$, then at 500 °C to CeO_2. Therefore, reduction of Ce(IV) to Ce(III) by nitrate occurs at first and then reoxidation of Ce(III) to Ce(IV) by nitrate occurs at higher temperatures. The same unexpected double valence change for cerium was observed during the thermal decomposition of $CeK_2(NO_3)_6$ [52].

3.2.5. Titanium oxide

Reactions of four titanium compounds of oxidation states (IV) and (III) were investigated by Kerridge and Cancela Rey [28] in molten $LiNO_3$–KNO_3 and in

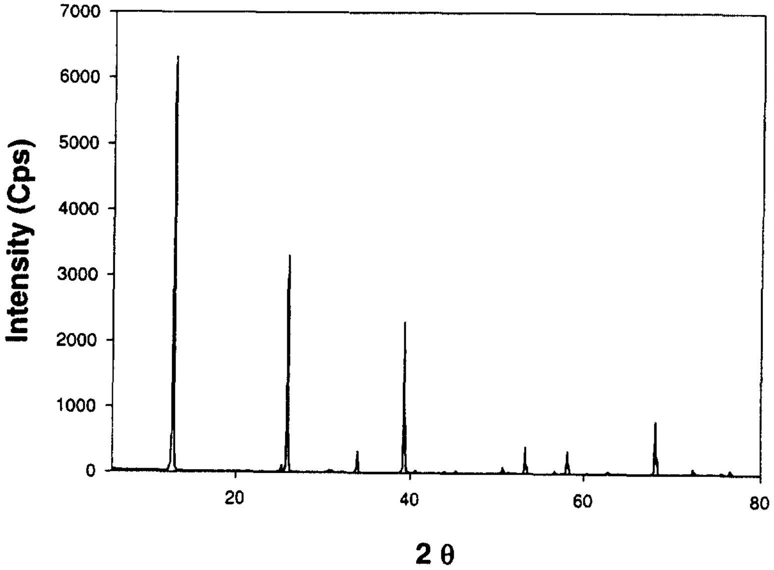

Fig. 2. XRD pattern of LaOCl prepared in molten $LiNO_3$ at 773 K.

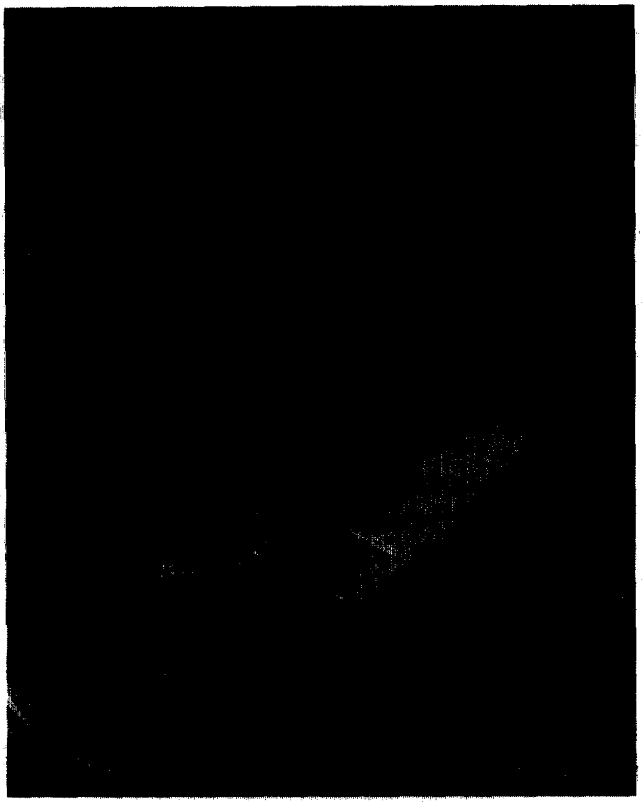

Fig. 3. SEM picture of LaOCl.

basic nitrate melt solutions containing sodium peroxide, monoxide or hydroxide. Titanium dioxide as anatase, and titanates of varying basicity were produced, depending on the base concentrations and temperature.

The preparation of TiO_2 and characterisation of the product focusing on its textural properties were studied by Harle et al. [53,54]. Titanium oxysulfate $TiOSO_4.2H_2O$ was used as the precursor salt and reacted with molten nitrates ($NaNO_3$–KNO_3 and $LiNO_3$–KNO_3 mixtures). The parameters of synthesis were optimised to obtain pure crystallised titanium dioxide TiO_2 with good textural properties. After annealing at 873 K, the specific surface areas were in the range of 80–100 $m^2 g^{-1}$ and had a mean pore radius close to 6 nm.

It follows from the examples presented above that fine dispersions of different oxides can be prepared from the nitrate melts, possessing the textural properties appropriate for their use as catalytic supports. Table 4 summarises some of the textural properties of simple oxides prepared from molten nitrates.

The starting compound, reaction conditions and composition of the melt have great impact on the properties of the oxides. An important problem in MS preparations is that sometimes there is a considerable amount of alkali metal cation impuri-

Table 4
Textural properties of transition metal oxides prepared at 673 K in molten nitrates

Oxide	Al_2O_3	CeO_2	TiO_2	ZrO_2
Specific surface area ($m^2\ g^{-1}$)	350	123	154	130
Pore volume ($cm^3\ g^{-1}$)	0.5	0.25	0.4	0.35

ties or residual species coming from the precursor salt. In order to get rid of these impurities while preserving the advantageous morphology of the product, the reaction conditions must be properly chosen.

3.3. Synthesis of multicomponent oxide systems

Most advanced materials for ceramics and catalysis are complex multicomponent systems, containing, for instance, solid solutions such as yttria-stabilised zirconia ceramics or fine dispersions i.e. mixed oxide catalytic supports on the base of alumina, doped with La, B, Ti and so on. Various methods of synthesis have been developed to achieve the desired chemical composition and morphology of the multicomponent inorganic materials. So-called soft chemistry, or Chimie Douce methods are used for the tailor-made preparations of solids with given properties, not available by classical solid preparation methods involving heating and grinding. Among them are the sol-gel process [55], intercalation-exfoliation reactions [56], and template-aided hydrothermal synthesis [57]. The common feature of these methods is that the solid products keep some memory about the precursors and additives used during the preparation. Being carried out at relatively low temperatures, soft chemistry routes often lead to metastable solids: homogeneous or heterogeneous nanodispersions; double hydroxides; or organic–inorganic hybrid materials. The low melting points of the nitrates can sometimes also be considered as a Chimie Douce medium. Molten nitrates were successfully used for the preparation of different classes of complex oxide systems, as described below.

3.3.1. Solid solutions versus mixtures of oxides

If, under the conditions of the MS reaction, two metal salts precipitate oxides, then the product of their simultaneous reaction may contain a mechanical mixture of the corresponding oxides, or a mixed oxide, or a solid solution. On the basis of about 20 combinations of metals tested, we can divide the experimental observations into four cases:

(1) Thermodynamically stable solid solutions and/or mixed oxides exist on the phase diagram of the corresponding oxide system. Those solutions were prepared in the MS reaction. The couples of such metals include Zr–Y, Zr–La, Zr–Ca, Ti–Ce(IV), Ti–Zr, Zr–Mn(IV), Zn–Cr(III), Mg–Al, Ca–Al and Co–Al.

(2) Solid solutions or mixed oxides exist on the phase diagrams, but could not be prepared in the MS reactions. Only mixtures of individual oxides were observed in the products. This is the case for Zr–Al, Zr–Pb(II), Zr–Zn, Al–Cu, Ti–Co, Ti–Ni, and Al–Ni pairs.

(3) Little solubility or mixed oxide formation on the equilibrium phase diagrams

were reported. However some metastable solid solutions were obtained from the MS reaction, which, after heating in air, decompose to a mixture of individual oxides. Such behaviour was observed for the Zr–Cu, Zr–Ru and Zr–Fe combinations.

(4) No solubility between the binary oxides exists according to phase diagrams. Indeed, only the mixtures of oxides were observed in the products of MS reaction. Zr–Ni and Zr–Co are examples of the independent simultaneous precipitation of two oxides.

The longest list of metal combinations corresponds to the first case (1), suggesting that molten nitrates are quite appropriate media for the preparation of mixed oxide systems, i.e. the interactions between various metal species in the melt are often strong enough to keep them together in the solid product.

Products belonging to the third case (3) can be considered as soft chemistry preparations, since the interactions here, between the metal species in the melt, lead to the formation of metastable solids, which cannot be obtained from the high temperature solid–solid reactions.

Note that this classification is based on experimental data which have been obtained using a rather narrow range of reaction parameters: temperatures (mostly 500 °C, sometimes 550 °C); precursor salts (always some chlorides or nitrates); the melt being, in almost all cases, equimolar $NaNO_3$–KNO_3. In fact, some metal combinations from the second set (2) can probably be transferred to the first set (1) by an appropriate choice of reaction conditions.

If the choice of synthesis parameters is important for the preparation of binary oxides, for the multicomponent systems it may determine the nature of the products obtained. For example, highly dispersed ($S \approx 140\ m^2\ g^{-1}$), green metastable solid Zr–Cu–O (atomic ratio Zr/Cu = 10) in which Cu(II) ions are dissolved in the tetragonal ZrO_2 lattice, could be prepared from the simultaneous reaction of $ZrOCl_2$ and $CuCl_2$ in molten $NaNO_3$–KNO_3 at 500 °C. However, if the corresponding Cu and Zr nitrates were taken as precursors, the mixture of ZrO_2 and CuO crystals was obtained.

Generally, to prepare a mixed oxide with an homogeneous distribution of the composing elements, the reaction parameters and precursor salts should be chosen in order to provide the simultaneous existence of the different dissolved species in the melt. This condition is better fulfilled if the corresponding precursor salts react with the melt in overlapping temperature ranges, as can be verified by preliminary thermal analysis of the reactions of the individual salts. By contrast, if the starting compounds react in separate temperature domains, then precipitation of one oxide may begin at the moment when formation of the other is already completed, or the dissolution of one starting salt may only commence when the other has already reacted. In the last case, formation of a crude mixture of oxides is more probable.

Below we discuss briefly the examples of MS preparations of mixed oxides, which present some interest for catalytic applications.

3.3.2. ZrO_2–Y_2O_3

Yttria-stabilised zirconia is a well-known ceramics material [58]. It also presents great interest for catalysis, since, due to the presence of dissolved yttrium, the tetragonal variety of ZrO_2 is stabilised, providing improved thermal stability, the advantageous properties of the zirconia support being virtually unchanged by ca. 3–10% of yttrium, introduced into the zirconia lattice.

Solid solutions ZrO_2–Y_2O_3 were prepared in Ref. [59] by means of the simultaneous reaction of zirconium oxychloride and yttrium chloride in the $NaNO_3$–KNO_3 melt at 450 °C. A tetragonal or cubic phase was obtained according to the yttrium content. The large specific area of the powders was observed (up to $120\ m^2\ g^{-1}$), suggesting their possible application for ceramics or catalysis.

A ZrO_2–Y_2O_3 solid was used as a support for hydrotreating reactions. Mo and NiMo oxides were deposited on the surface and sulfided. Catalytic activities in model hydrotreating reactions were found to be higher than those obtained on alumina-supported catalysts. This result was correlated to a better dispersion of the active phase on ZrO_2–Y_2O_3 support [60,61].

3.3.3. ZrO_2–Al_2O_3

The preparation of alumina–zirconia dispersions was made by the simultaneous reaction of hydrated $ZrOCl_2$ and $AlCl_3$ at 450 °C, using different nitrate melts [62,63]. It was found that the presence of alumina delays the growth of the zirconia particles, stabilising its tetragonal modification.

Our results on the Zr–Al oxide dispersions obtained from nitrate melts show that already at a content of ca. 10–20 mol.% of alumina in the solid, its properties as a catalytic support being similar to those of pure alumina, probably because of the difference in the dispersion of the two oxides. Zirconia forms crystallites of 4–5 nm size, whereas alumina is almost amorphous, the XRD size of its particles being below 2 nm. The alumina microparticles are apparently dispersed on the surface of zirconia crystallites, thus covering it almost completely already at an alumina content as small as 10%. For that reason, the gain of textural properties provided by aluminium seems to be rather useless, since the solid obtained loses the eventual advantages of a zirconia support.

3.4. Ternary oxides and oxosalts

If one of the precursors precipitates an oxide and another provides an oxoanion soluble in the melt, the formation of ternary or more complex stoichiometric compounds is possible. Abood and Kerridge [21,33] reported precipitation of calcium chromate and lithium periodates. Molybdenum-based unsupported catalysts represent an important class of industrial oxidation catalysts. We attempted to prepare several of these transition-metal-doped molybdates and to characterise them by XRD and UV spectroscopy [64].

The reaction of ammonium heptamolybdate and nickel nitrate in the molten nitrate bath at 500 °C led to the formation of crystalline $NiMoO_4$. Iron and cobalt nitrates gave more complicated mixtures of crystalline products, sometimes including alkali metals: $K_3FeMo_4O_{15}$; $NaFe(MoO_4)_2$; $Fe_2(MoO_4)_2$; $NaCO_{2.31}(MoO_4)_3$; and $CoMoO_4$. Bismuth molybdate is used as a catalyst for the production of acrylonitrile via ammoxidation of propene (SOHIO process). A bismuth molybdate has been prepared in molten nitrates at 773 K from the simultaneous reactions of hydrated $Bi(NO_3)_3$ and $(NH_4)_6Mo_7O_{24}$. The product corresponds to the Bi_2MoO_6 phase, as shown in Fig. 4. A preferable orientation along the *b*-axis is obtained (peaks corresponding to (020) and (060) planes are the more intense). This specific morphology is confirmed by the scanning electron microscopy (SEM) picture (see Fig. 5). Crystals with an elongated shape are observed.

3.5. The synthesis of phosphates

The solubility of alkali metal phosphates and the acidobasic transformations of phosphate ions in nitrate melt were studied. Diphosphates and higher polyphosphates were decomposed into monophosphate in the nitrate melt [30,65]. Various ternary and more complex mono- and diphosphates can easily be synthesised in molten nitrates, by the interactions of monophosphates and diphosphates dissolved in the melt with the appropriate metal species.

Initially, we reported the preparation of a $Na_{1.8}K_{0.2}Zr(PO_4)_2$ lamellar structure under mild conditions provided by molten nitrates [66]. Zirconium oxychloride and sodium mono-H orthophosphate reacted in the $NaNO_3$–KNO_3 mixture. After reaction at 773 K, a solid corresponding to the α-ZrP phase was obtained. On the basis of thermogravimetric analysis, the following equations involving a complexation

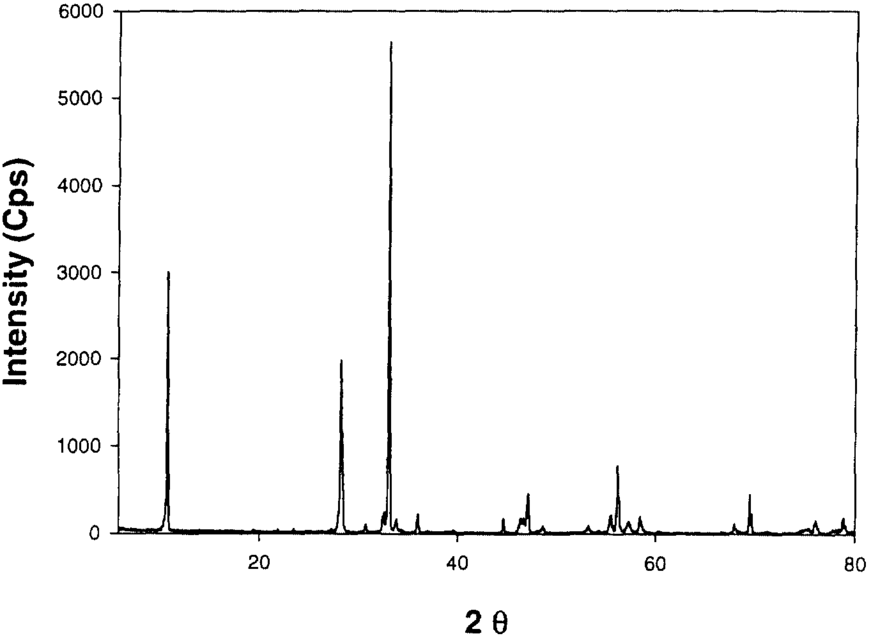

Fig. 4. XRD pattern of Bi_2MoO_6 prepared in molten nitrates at 773 K.

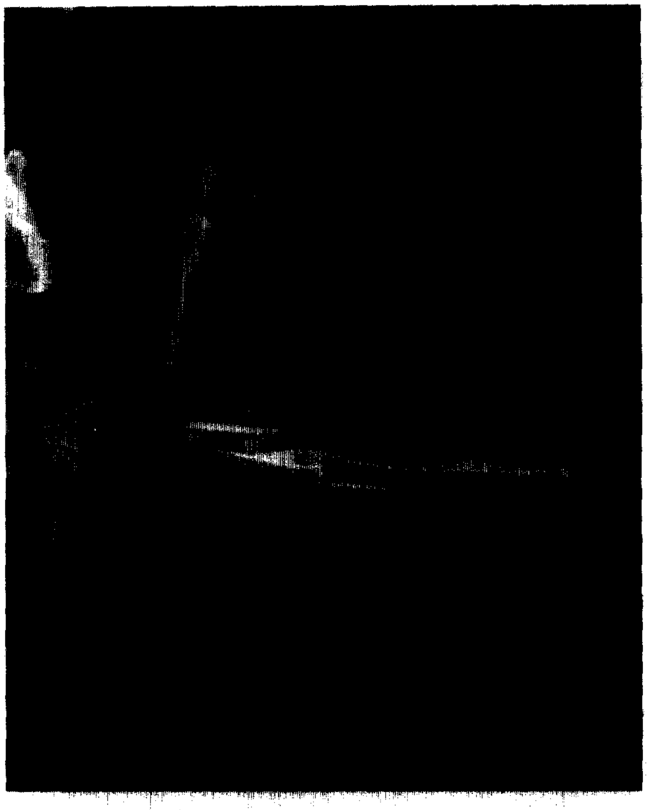

Fig. 5. SEM picture of Bi_2MoO_6.

step and a reaction step were proposed:

$$ZrO^{2+} + 2HPO_4^{2-} \rightarrow ZrO(HPO_4)_2^{2-}, \tag{12}$$

$$ZrO(HPO_4)_2^{2-} \rightarrow Zr(PO_4)_2^{2-} + H_2O. \tag{13}$$

Potassium zirconium phosphates, such as lamellar $K_2Zr(PO_4)_2$ or NASICON $KZr_2(PO_4)_3$ phosphates, were also prepared [67].

Zirconium hydrogen phosphate, $Zr(HPO_4)_2.2H_2O$, as an ion exchanger, was found to be stable to 350 °C in $NaNO_3$–KNO_3. At higher temperatures, hydrogen was replaced by alkali metal ions [68].

A recent extensive study showed that a large number of pure microcrystalline phosphates are available through the nitrate melts. The products usually include stoichiometric amounts of alkali metal cations. Among the products obtained are numerous known phosphates, such as natrium zirconium super conductor (NASICON)-derived compounds of Ti, Zr and Hf, or $AMPO_4$ ferroelectrics ($A=$ Na, K, Cs; $M=$Ca, Sr, Ba, Pb, Zn), as well as several novel phases. Only Na, K and Cs nitrates can be used for these preparations, since ammonium phosphate reacts with molten $LiNO_3$ leading to the water-insoluble Li_3PO_4. The reaction temperature and relative amounts of precursors are the important parameters [67]. The P/M atomic ratio in the reaction mixture needed to obtain pure mixed phosphate phases should be considerably above the stoichiometry of known phosphates for the element, M. As a rule, the ratio P/M=4 was sufficient to prepare pure mixed phosphate phases. The amount of nitrate was less important but must also provide a large excess. Elevated temperatures (above 550 °C) or doping of the reaction mixtures with bases often led to decomposition of phosphates with the precipitation of oxide of an element, M (see discussion in Section 4.1). Transition metal phosphates prepared in molten nitrates usually present highly oriented morphologies, as illustrated in Fig. 6, in the case of nickel potassium phosphate.

3.6. Synthesis of lamellar Zr–Na sulphate: new ion exchanger and intercalation host

As an example of solid synthesis, where the molten nitrate method acts as a soft chemistry route, we consider the recent preparation of the lamellar non-stoichiometric sulphate of Zr–Na.

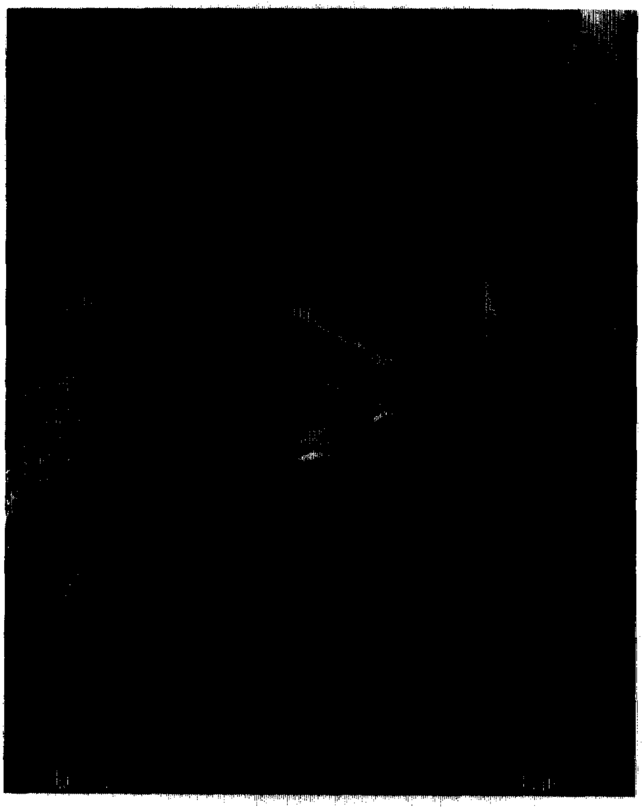

Fig. 6. SEM picture of $K_2Ni_4(P_2O_7)_2(PO_4)$ prepared in molten KNO_3 at 773 K.

It was reported earlier [42,46] that the reaction of $Zr(SO_4)_2$ in molten nitrate gives ZrO_2 at 500 °C, but, due to the complexing properties of sulphate, the reaction is difficult to accomplish. It appears that an intermediate product of this reaction, which can be isolated at lower temperatures, presents independent interest as a new lamellar compound with ion-exchanging properties and the possibility to be intercalated with organic amines.

The product (called NaZ) was obtained by reacting $ZrOCl_2$ in molten $NaNO_3$–Na_2SO_4 (molar ratio = 4/1) melt at 673 K. The chemical composition of the product corresponds with the composition $ZrS_{0.33}Na_{0.21}O_x$.

A strong line at $d = 1.28$ nm and several smaller peaks were observed in the X-ray diffraction pattern of NaZ (Fig. 7). Consistent with the assumption of a lamellar structure of NaZ, the SEM photograph (Fig. 8) showed oriented morphology, the crystals forming agglomerates of sheets of ca. 100 nm thickness. On transmission electron microscopy (TEM) micrographs, poorly ordered lamellar structures were observed, the distance between the layers coinciding with the XRD value.

The infra-red (IR) spectrum of NaZ showed strong absorption lines in the sulphate stretching-vibrations region, at 1241, 1084 and 1027 cm^{-1}, corresponding to the different vibrations of bridging sulphates in a bulk-like sulphate phase. Heating of NaZ in air at 873 K transformed the IR spectra to that corresponding to air-hydrated sulphate on zirconia, with a broad absorption peak at 1150 cm^{-1}. At the same time, XRD showed that after heating, NaZ was completely transformed to the tetragonal ZrO_2.

The NaZ solid showed ion exchange properties. Na^+ cations were reversibly

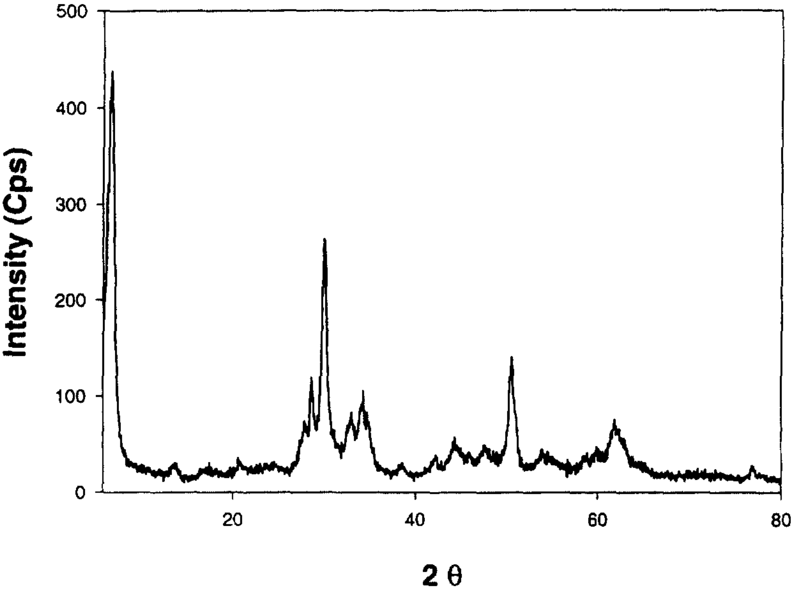

Fig. 7. XRD pattern of NaZ compound.

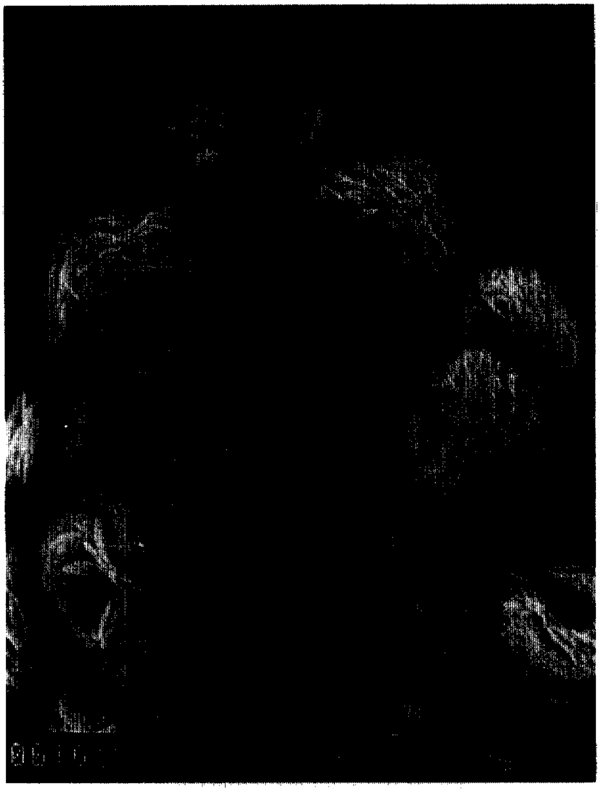

Fig. 8. SEM picture of NaZ.

exchanged with monovalent (K^+) or bivalent (Ba^{2+}) cations by stirring the NaZ suspensions in 1 M solutions of the corresponding nitrates. In the ion-exchanged solids, KZ and BaZ interplanal distances were, respectively, 1.152 and 1.248 nm. The treatment with diluted HNO_3 gave the protonic HZ form with an interlayer distance of 1.097 nm, with the broadening and decrease of intensity of XRD peaks suggesting the disordering of the layer packing. ^1H magic angle spinning (MAS) spectrum of the HZ solid was dominated by a band at $\delta = 4.84$. whereas that of NaZ consisted mostly of bands of Zr–OH groups ($\delta = 3.59$), adsorbed water ($\delta = 0.0$) and more basic OH groups ($\delta = -2.82$). The enhanced acidity of the HZ sample was revealed in its high specific activity in the model reaction of isooctane cracking reaction under nitrogen atmosphere, being for HZ twice greater than that of the protonic form of zeolite Y under the same conditions.

The NZ solid was obtained from a 24 h reflux of the HZ sample in pure *N*-pentylamine, under a nitrogen atmosphere. This retained the lamellar structure of the parent HZ compound, but the interplanal distance was 1.946 nm, being increased by ca. 0.66 nm, due to the intercalation of amine between the layers. The intercalation with *N*-pentylamine appears to be reversible, since washing of NZ by 1 M NaOH restored the initial XRD pattern of NaZ.

4. Synthesis of supported catalysts

As demonstrated above, the molten salt technique can produce, at a relatively low temperature, highly divided oxides with interesting textural properties. Many industrial catalysts are composed of supported oxides. The most common method for their preparation involves two steps, i.e. the preparation of the support and then the dispersion of the active species or its precursor onto the surface. Usually the supports are silica or alumina, but considerable interest is devoted to other oxides such as those of Ti, Zr or Nb [69]. The supported species are often those of transition metals (Mo, V and so on) dispersed at the surface of the support in the form of oxoanions or small oxide clusters.

The oxoanions of the transition metals of V–VI groups are formed in the nitrate melt (see Table 3). It was found that the interaction of such oxoanions with the particles of oxides (simultaneously precipitated in the same melt) could yield not only ternary compounds, but, in certain cases, multicomponent dispersed systems, which possess all the properties of supported catalysts, i.e. a dispersed oxide (support) with some other metal species grafted on its surface (active phase). This way the molten salt technique provides a one-step route for the preparation of supported catalysts, as discussed below.

4.1. One step preparation of supported catalysts

4.1.1. Mo on zirconia

The simultaneous reaction of hydrated $ZrOCl_2$ and $(NH_4)_6Mo_7O_{24}$ in $NaNO_3$–KNO_3 gave fine dispersions, containing tetragonal zirconia of ca. 5 nm size, with the oligomolybdate species anchored on its surface [70]. The properties of these solids were in many respects similar to those reported for MoO_3/ZrO_2-supported catalysts. However, the solid obtained demonstrated much higher specific surface areas compared with those of pure or yttria-stabilised zirconia prepared either by the same MS method or by conventional aqueous techniques. Specific surface areas as high as 220 $m^2 g^{-1}$ could be obtained for the Mo–Zr–O solids. Moreover, the stability of the textural properties to calcination in air at temperatures up to 1073 K was also considerably improved due to formation of a metastable monolayer of molybdate on the zirconia surface, as discussed in Ref. [71]. Molten salt, Mo–Zr–O, preparations after subsequent sulfidation showed enhanced activity in the model hydrotreating reactions [70].

4.1.2. Genesis of the supported systems

Consideration of the interactions between the transition metal species in the melt may explain the genesis of the supported catalyst with the example of the Zr–Mo system. With the simultaneous reaction of both Zr and Mo salts in molten nitrates, surface interactions between the growing particles of ZrO_2 and molybdate anions occur [72]. As in aqueous chemistry, grafted mono- or polymolybdate species can be obtained at the surface of the solid since molybdate can polymerise on the surface of growing zirconia nuclei. By analogy with aqueous chemistry, the degree of polymerisation depends on the acidobasicity of the medium. Such polymolybdate species locally stop the growth of the ZrO_2 nuclei and remain on the surface of the solid product. Both bulk phases MoO_3 and $Zr(MoO_4)$ are unstable and react in the molten nitrate, so that formation of these species is excluded. Only superficial polymolybdates are stable in the melt.

It is noteworthy that the starting compound for the preparation of supported Mo/Zr oxide catalysts in the nitrate melt may be $(NH_4)_6Mo_7O_{24}$, MoO_3 or Na_2MoO_4. In all three cases, very similar solids were obtained, only differing slightly in their specific surface area, otherwise having identical ultra-violet(UV)-visible, IR spectra and XRD patterns [72]. If the starting compound was MoO_3 then it reacted as a L–F acid, with the rupture of Mo–O–Mo bonds:

$$x\mathrm{MoO_3} + y\mathrm{O^{2-}} \rightarrow \mathrm{Mo}_x\mathrm{O}_{3x+y}^{2y-}. \qquad (14)$$

In contrast, sodium monomolybdate reacted as a base. Formation of the Mo–O–Mo bonds occurred due to polymerisation:

$$x\mathrm{MoO_4^{2-}} \rightarrow \mathrm{Mo}_x\mathrm{O}_{3x+y}^{2y-} + (x-y)\mathrm{O^{2-}}. \qquad (15)$$

However, the final product was the same, since it is determined by the basicity of the melt. Altering several parameters such as reaction temperature, and the nature of the nitrate melt can vary the properties of the product. We can summarise these effects as follow: the increase of the melt basicity due to temperature increase or admixtures of bases into the melt diminishes the degree of polymerisation of superficial polyoxospecies. Then, it provokes partial dissolution of Mo from the solid to the melt in the form of soluble oligomers (alkali metal mono- di- and trimolybdates).

4.1.3. *Other supported catalysts*

The encouraging results mentioned above were generalised to other oxoanions and oxides; V, Nb, W, Cr. Results similar to those for the Zr–Mo combination have been obtained for zirconium with V, W, Nb, and Cr [73], as well as for the Al–Mo pair Fig. 9.

As observed in the case of Mo, zirconia particles can accommodate at the surface a certain amount of the oxoanions of a doping element. Above this loading, some part of the dopant was wasted, remaining in the melt as a soluble alkali metal oxosalt. The thermal stability of the doped zirconia depends on the nature of the added transition metal and is related to the decomposition temperature of the superficial species [74].

4.1.4. *Oxide dispersion versus bulk compound*

A question arises: why, in some cases, does the simultaneous MS reaction of metal species lead to crystalline ternary salts, whereas in others, fine oxide dispersions are formed?

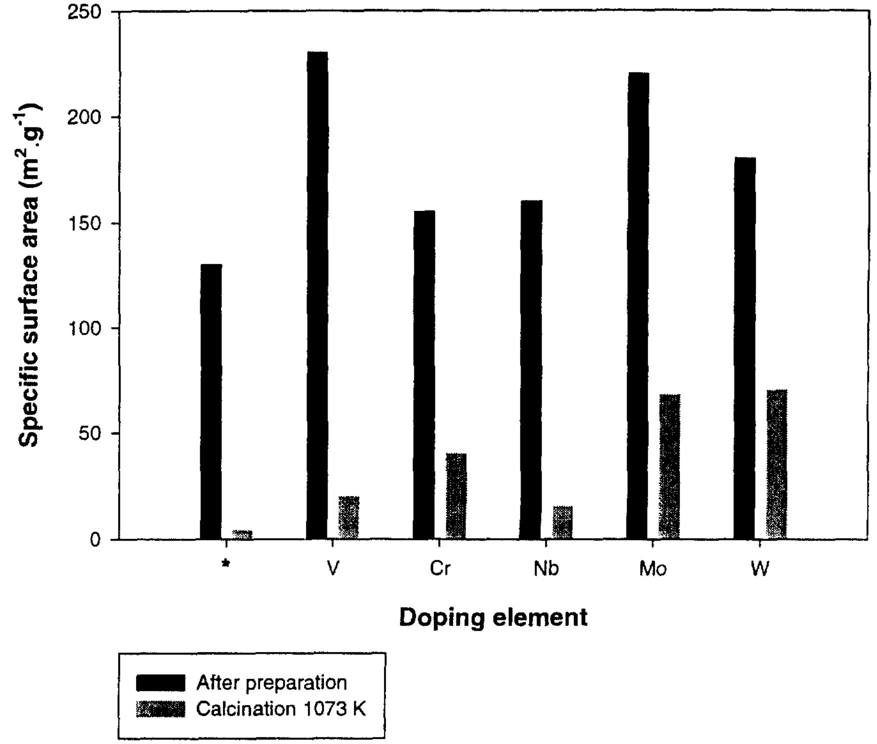

Fig. 9. Specific surface areas of zirconia doped and undoped (*) samples after preparation and calcination at 1073 K.

From Table 1, one can estimate the numerous possibilities offered for the simultaneous synthesis, just by combining the precursors. From this variety of cases, several combinations have been tried, presenting potential interest for catalysis. The results for preparations in molten $NaNO_3$ at 500 °C are sketched in Table 5. Of course the nature of products can sometimes be changed with temperature or with the melt basicity. However, a general trend can clealy be seen: low soluble covalent oxides

Table 5
Phase composition of products issued from the simultaneous reactions of precursor alts in molten $NaNO_3$-KNO_3 at 500 °C

Oxoanion(s) oxide	SO_4^{2-}	MoO_4^{2-}	VO_4^{3-}	PO_4^{3-}
Al	Al_2O_3	Al_2O_3	Al_2O_3.	Al_2O_3
Zr	ZrO_2	ZrO_2	ZrO_2	$Na_2Zr(PO_4)_2$
Ti	TiO_2	TiO_2	TiO_2	$Na_2Ti(PO_4)_2$
Zn	ZnO	ZnO	$NaZnVO_4$	$NaZnPO_4$
Mg	MgO	$MgMoO_4$	$Na_4Mg(VO_4)_2$	$Na_4Mg(PO_4)_2$
Ni	NiO	$NiMoO_4$	$NaNiVO_4$	$NaNiPO_4$
Ca	$CaSO_4$	$CaMoO_4$	$NaCa_4(VO_4)_3$	$NaCaPO_4$

and weakly complexing oxoanions yield oxide dispersions, whereas combinations of strongly complexing oxoanions and more soluble ionic oxides are more favourable for the formation of bulk compounds.

These results can be qualitatively explained from consideration of L–F acidobasic interactions and solubility equilibria.

Let us suppose that a bivalent oxide, MO, is in equilibrium with the nitrate melt. The solubility of an oxide is described by the equilibrium:

$$MO \Leftrightarrow <M^{2+}> + <O^{2-}> \quad K^1. \qquad (16)$$

If, at the same time, an oxoanion, A^{2-}, is present in the melt, there is also an equilibrium for complexation (or that of solubility of MA):

$$<M^{2+}> + A^{2-} \Leftrightarrow MA \quad K^2. \qquad (17)$$

The result of the overall reaction, i.e. the stability of a salt, MA, towards the L–F reaction with the melt is described by the equilibrium:

$$MA + <O^{2-}> \Leftrightarrow MO + A^{2-} \quad K^3. \qquad (18)$$

Here the brackets imply that we do not make any suppositions about the exact structure of the species present in the melt, which can be nitrato complexes, ion associates and so on, but consider only the «effective donation» of oxygen anions from nitrate to the species of metal, M.

It is evident that $K^3 = K^2/K^1$, which means that decomposition of a ternary compound leading to the oxide dispersion is favoured by poor solubility of an oxide and by a low stability constant (high solubility) of the MA compound. Note that it is supposed that oxoanion, A, does not undergo any chemical interactions with the melt, which is probably the case for the species listed in Table 3.

The low, long-term stability of molten nitrates creates difficulties for the direct determination of the solubility of weakly soluble metal oxides therein. No experimental solubility scale in molten nitrates has yet been published. However, it seems reasonable that the sequence of relative solubility of oxides in molten nitrates should be somewhat similar to that in molten chlorides, since both melts are highly ionic, so that the solubility must be determined by the similar electrostatic interactions of dissolved species in the melt. If the sequence of relative solubility of metal oxides in molten nitrates coincides with that in molten chlorides [10], then the solubility decreases in the range; $Ca > Mg \approx Zn \approx Ni > Ti \approx Zr \approx Al$.

Therefore, Ca, which forms a rather soluble CaO oxide, gives, in all cases considered, some ternary salts, whereas Al (poorly soluble Al_2O_3) only yields oxide dispersions. The above discussion also allows understanding as to why the less complexing sulphate gives supported dispersions, whereas strongly complexing phosphate forms ternary bulk compounds with almost all the metals tried. We should emphasise again that formation of the oxide or ternary salt depends not only on the reacting species but also on the conditions of reaction. Lower preparation temperatures favour formation of bulk compounds: lamellar Na–Zr phosphate (ternary salt) was isolated at 400 °C, whereas at 500 °C, the product of reaction is ZrO_2 with some sulphate grafted on its surface (oxide dispersion). The change of alkali metal cation and, therefore, of the melt basicity can also switch between different kinds of products, especially in the borderline cases. For example, the action of Ni and Mo salts in $NaNO_3$ gave, at 500 °C, $NaMoO_4$ compound. The same reaction in the strongly basic $LiNO_3$ led to the NiO oxide dispersion.

4.2. *Mixed oxide species on a support*

The situation when three metal species react in the melt requires consideration of triple interactions of species and cannot be rationalised on the basis of a simple qualitative model, as made above for the two component products. However, the importance of multicomponent systems in catalysis encouraged us to study such syntheses. Multicomponent-supported oxides represent a large class of catalysts. After sulfidation, NiMo, CoMo or NiW oxides dispersed on alumina are commonly used in refineries for hydrotreating.

The simultaneous molten nitrate reactions of Ni, Mo and Zr precursor salts allow the preparation of mixed-dispersed Ni–Mo phases on a support. As previously shown in Table 3, nickel alone precipitates NiO and when it is mixed with molybdenum, it precipitates $NiMoO_4$. However, due to some favourable interaction with zirconia during the synthesis in the melt, the XRD-amorphous NiMo oxide species spread over the surface of zirconia have been produced in the MS reaction. Then, we attempted to prepare, in molten nitrates, solids of general composition: MMo/ZrO_2 and MW/ZrO_2 with M = Fe, Co, Ni. Simultaneous reactions of (Ni, Co, Fe), (Mo, W) and Zr precursors produced fine dispersions [64], showing only the presence of tetragonal (T) zirconia and traces of its monoclinic (M) form in the XRD patterns. Even after calcination at 800 °C, no extra phases appeared. Therefore, the presence of (Mo, W) species in the reaction mixture hinders the formation of the bulk oxides of Fe, Co and Ni, which would be formed if the corresponding salts reacted alone or in the mixture with Zr(IV) salts. No bulk molybdates (tungstates) of VIII group metals have been observed. Therefore, the role of triple interaction is essential, since the products were different from any superposition of those from binary interactions.

Moreover, a mixture of NiO and ZrO_2 crystals previously prepared in molten nitrate was introduced in the reactive nitrate melt, which contained dissolved molybdate. As a result, NiO reflexes disappeared from the XRD pattern. Nevertheless, the initial amount of Ni remained in the solid. Thus, the molybdate species from the nitrate melt reacted with Ni oxide, leading to the spreading of the resulting Ni–Mo-mixed oxospecies over the surface of the zirconia support. Finally the product of this two-step molten salt synthesis was similar to the product of simultaneous reaction of three starting compounds of Ni, Mo and Zr.

It is worth noting that the textural properties of the solids produced in the molten salt reactions of three precursors as described above, were even better than those from pairs of metals. Table 6 gives the specific surface areas of different MS samples versus the calcination temperature. Compared with the classical preparations of zirconia supported systems, the surface areas are two times higher and thus indicate

Table 6
Specific surface areas ($m^2 g^{-1}$) of the zirconia-supported samples versus calcination temperatures (adapted from Ref. [64])

	Calcination temperature (K)		
	573	873	1073
Sample	Specific surface area ($m^2 g^{-1}$)		
$CoMo/ZrO_2$	232	123	45
$NiMo/ZrO_2$	250	199	150
$FeMo/ZrO_2$	235	151	58
Mo/ZrO_2	220	150	60
Ni/ZrO_2	130	91	4
ZrO_2	126	80	2.5

the determinant role of the dopants on the growth of zirconia crystallites in the melt. NiMo, CoMo and FeMo pairs provide even more pronounced stabilising effects than sole Mo dopant.

UV–visible spectroscopy suggested, in these solids, the formation of the mixed oxospecies between Ni (Fe, Co) and Mo, where the elements of VIII group are attached to molybdate by M–O–Mo bonds, or one may view this as molybdate entering the inner coordination sphere of M ions.

This preparation method generates free space for adding the more active phase in a conventional manner. As the result, well-dispersed, highly loaded catalysts can be prepared with this new technique. Hydrosulferization (HDS), hydrogenation (HYD) and hydrodenitrogenation (HDN) activities two times as great as those observed on a commercial catalyst can be achieved by the use of catalysts prepared from molten salts [64].

This technique has been extended for the preparation of other oxide systems of potential interest in catalysis, e.g. Ni–Mo supported on Al_2O_3 and MgO, or mixed Bi–Mo oxospecies supported on zirconia. In all these cases, XRD-amorphous mixed oxospecies spread over the surface of highly dispersed, support oxide particles. These results clearly illustrate the versatility of molten nitrates for synthesising complex oxide systems.

5. Managing the reaction

As already mentioned, even slight modification of the melt composition by active admixtures may, in some cases, considerably change the reactivity of the precursor salts. As discussed above for the preparation of simple oxides, titania or ceria with enhanced textural properties can be obtained by using additives such as nitrites or Na_2O.

A disadvantage of the use of molten nitrates for preparations of solids is the production of heavily pollutant NO_x gases during the reaction. One possibility to solve this problem is the introduction of carbonates in the nitrate melt. Due to the high reactivity of the carbonate ion in comparison with that of nitrate, we can expect that the carbonate will act as the oxygen source, reducing nitrate decomposition. Carbonates may also act as a textural modifier, similar to preparations performed in aqueous media [75]. So, we investigated a mixture of KNO_3–$NaNO_3$–Na_2CO_3 as a reaction medium. Various contents of Na_2CO_3 have been added to the nitrate mixture and reacted with a $ZrOCl_2$ precursor salt.

The gases produced during the reaction were analysed using a mass spectrometer. When carbonates were added, the reaction pathway changed and the amount of NO_2 was drastically reduced by factors of about 40. Chemical analysis indicated that the samples contained residual carbonates (0.2–0.6 wt.%). The morphology of zirconia was changed, such that, when the spherical agglomerates were observed by scanning electron microscopy when nitrates were used alone, they were transformed by carbonate admixture into a "cheesehole" structure. Finally, the textural properties were greatly affected, with a significant increase of the mean pore size and the porous volume, with little modification of the specific surface area (varying from 132 up to 144 $m^2 g^{-1}$) being observed (see Fig. 10).

Another possibility to modify the properties of the solids obtained in MS reactions is to add some strongly complexing species. For example, fluoride ions are known to give stable complexes with polyvalent metal cations in the nitrate melts [76], thus affecting the solubility of metal species and, consequently, the morphology or even the chemical composition of the precipitate.

The influence of small admixtures of fluoride on the properties of molten salt

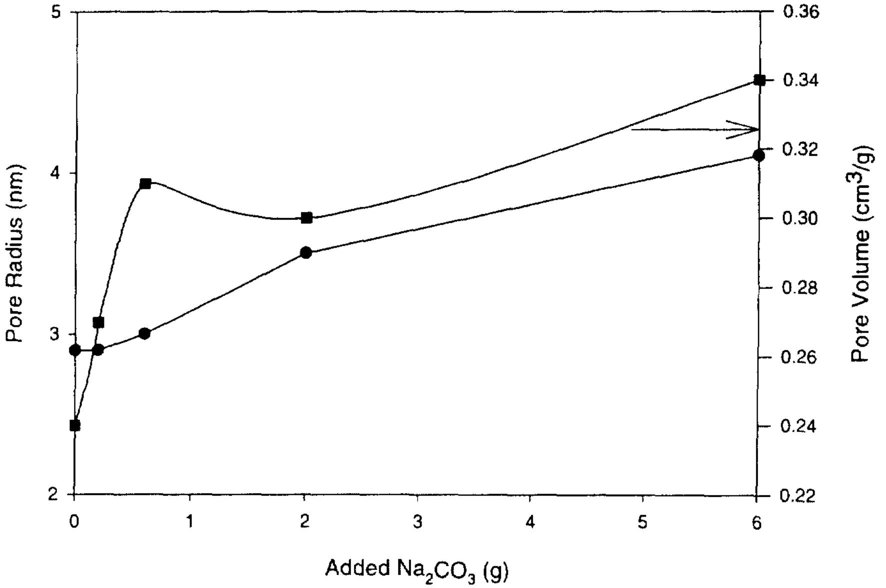

Fig. 10. Modification of the texture of the zirconia with the amount of carbonate in the melt added to 10 g of nitrate.

preparations of zirconia was studied in Ref. [77]. The series of zirconia samples was prepared in the low-melting $NaNO_3$–KNO_3 mixture, doped with different amounts of ammonium hydrogen fluoride ranging from 0.05–1 wt.% of NH_4HF_2 in the reaction mixture.

The results of XRD and the measurements of textural properties showed that even small amounts of fluoride drastically changed the properties of zirconia obtained, strongly promoting the growth of the thermodynamically stable M phase. At the same time, the mean radius of the pores gradually increased with the amount of fluoride, whereas the specific surface area and pore volume versus fluoride content passes through a maximum.

It was concluded that fluoride acts as an efficient mass transfer agent, accelerating recrystallization and growth of zirconia particles. Apparently, solubilisation of Zr species by fluoride occurs, in the form of anionic fluoride complexes. If the reaction was carried out at the 10-fold excess of NH_4HF_2 relative to Zr, pure Na_3ZrF_7 phase was formed, suggesting the solubilisation of Zr(IV) as ZrF_7^{3-} species:

$$ZrO_2 + 7F^- \Leftrightarrow ZrF_7^{3-} + 2O^{2-}. \tag{19}$$

If the amount of fluoride is small, ZrF_7^{3-} ions remain dissolved in the melt, just accelerating the recrystallisation of zirconia particles.

6. Conclusion

It appears from this review article that molten nitrates offer numerous possibilities for the synthesis of oxide compounds. Simple oxides, solid solutions or ternary salts can easily be obtained at relatively low temperatures. Moreover, this method provides a one-step preparation for a large number of complex-supported systems. The catalytic properties of these solids have been briefly investigated in several model reactions, but obviously the other applications can be envisaged. The resulting products are usually of high surface area and thermally more stable than those prepared by other methods. The use of molten bath additives, such as nitrites, alkali metal oxides, carbonates or fluoride, modifies the reaction rates and mechanism and/or the texture of the products. Then, it is possible to adapt the reaction parameters to a specific product.

Molten nitrate synthesis method is not commonly employed for the preparation of inorganic materials. However, it seems to be a simple, low cost, highly reproducible and efficient technique that is still virtually unexplored.

Acknowledgements

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