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Review
Synthesis and features of binary cobaltite spinels

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The main developments in the synthesis of cobaltites are surveyed. Solid state reactions between oxides, thermal decomposition of mechanical mixtures of transition metal salts, the use of complex compounds as precursors, mechanochemical synthesis, deposition of cobaltites on supports and cobaltite synthesis by thermal treatment of coprecipitated compounds are discussed and the specific advantages and disadvantages of each method pointed out. The binary spinel cobaltites find applications as materials in many fields, their main importance being as catalysts. In order to achieve high specific surface area, cobaltite synthesis by thermal treatment of coprecipitated precursors proves to be the most promising method. Different kinds of precursors are regarded. Transition metal basic salts are promising for the synthesis of binary mixed oxides and, in particular, of cobaltites. The conditions suited by the coprecipitated precursors for the synthesis of cobaltites with preset properties, such as high-dispersity, homogeneity, a definite stoichiometry and a low impurity content, are indicated. Special attention is paid to hydroxidecarbonates. Their use as precursors ensures these demands for the final product and also evolution of toxic gases during the thermal decomposition is avoided.

1. Introduction

The spinel Co_3O_4 has a high catalytic activity with respect to a number of complete oxidation reactions [1–9]. This is ascribed to the high mobility and the low binding energy of surface oxygen in this oxide [3, 6–10]. The binary cobaltites have similar behaviour [1, 11–13]. Some authors consider that this class of compounds and some transition metal mixed oxides are more stable than the noble metals against catalytic poisons [14]. The cobaltites are supposed to be suitable substitutes for platinum and palladium in catalytic combustion processes. Their use as catalysts and oxide electrode materials [15–21] is the main reason for the enhanced interest in the synthesis and properties of this type of compounds.

The catalytic properties of spinel mixed oxides have been studied in several model reactions: oxygen isotope exchange, hydrogen, methane and toluene complete oxidation [22–24]. The activities of some binary spinel cobaltites in these three model catalytic reactions are presented on Figs 1 and 2 and the activation energies are collected in Table I. Their activity depends on the metal–oxygen binding energy and the amount of reactive oxygen on the surface. The highest oxidation rate is observed on the cobaltites of copper, zinc and nickel. The studies of different authors have proved that water vapour influences the reaction rate insignificantly, while carbon dioxide depresses the reaction in the case of $CaCo_2O_4$. This is explained by poisoning of the surface as a result of partly irreversible adsorption [22]. Although cobaltites are generally accepted as combustion catalysts, the selective oxidation of propene to acrolein on a copper–cobalt spinel mixed oxide catalyst has also been investigated [25].

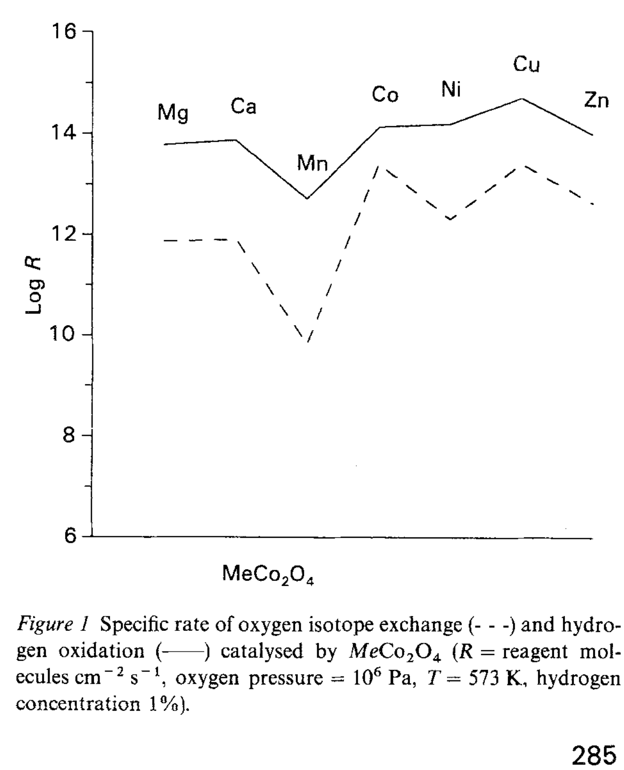

Figure 1 Specific rate of oxygen isotope exchange (- - -) and hydrogen oxidation (——) catalysed by $MeCo_2O_4$ (R = reagent molecules cm^{-2} s^{-1}, oxygen pressure = 10^6 Pa, $T = 573$ K, hydrogen concentration 1%).

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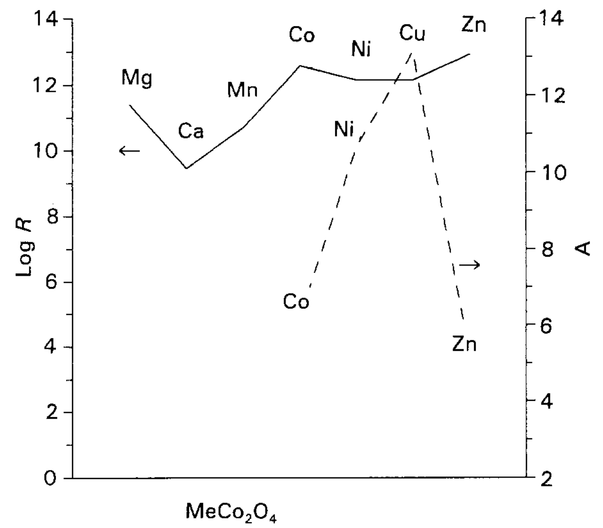

Figure 2 Specific rate of: (a) methane oxidation (——) catalysed by $Me\mathrm{Co_2O_4}$ (R = reagent molecules cm^{-2} s^{-1}, pressure = 10^5 Pa, $T = 573$ K, methane concentration 1%); (b) toluene oxidation (- - -) catalysed by $Me\mathrm{Co_2O_4}$ (A = activity, [moles g^{-1} s^{-1}] $\times 10^7$, $T = 510$–545 K).

TABLE I Activation energies for different cobaltites in catalytic reactions [22, 24]

Cobaltite	E_a, [kcal mol^{-1}]			
	Oxygen isotope exchange	Hydrogen oxidation	Methane oxidation	Toluene oxidation
$MgCo_2O_4$	18	11	27	
$CaCo_2O_4$	9	11	29	
$MnCo_2O_4$	17	12	28	
Co_3O_4	16	10	16	8.1
$NiCo_2O_4$	21	17	24	15.6
$CuCo_2O_4$	25	15	21	12.9
$Cu_{0.8}Co_{2.2}O_4$				8.9
$Cu_{0.5}Co_{2.5}O_4$				11.6
$Cu_{0.2}Co_{2.8}O_4$				13.4
$ZnCo_2O_4$	18	14	16	

Transition metal mixed oxides are also known as precursors of other important catalysts – for hydrogenation, olefin metathesis, etc. [41]. This determines the interest in the catalytic behaviour of these compounds towards oxidation processes in general, as well as in their synthesis.

The cobaltites of IVth period metals of the Periodic Table have been studied in detail, as have Mg and Ca cobaltites [1, 13, 22]. Cations with different sizes and charges may enter the spinel lattice. The oxygen anions are ordered in a close cubic array, while the cations fill one half of the octahedral and one eighth of the tetrahedral positions. The unit cell $A_8B_{16}O_{32}$ contains 32 anions, which, in the ideal case, are arranged in the densest cubic packing and form 64 tetrahedral and 32 octahedral sites, 8 tetrahedral (A positions) and 16 octahedral (B positions) being occupied by cations (Fig. 3). The general chemical formula is AB_2O_4.

A non-ideal spinel structure is formed as a result of the shift of anions from the sites of the face-centered cubic lattice in direction to the nearest tetrahedral ion. Normal, inverse and mixed spinels are distinguished, depending on the cation distribution among the available positions. In the case of a normal distribution in a binary spinel $A[B]_2O_4$, the two B cations occupy the octahedral, while the A cations are on tetrahedral sites in the lattice. In inverse $B[AB]O_4$ spinels, both A and B cations are distributed statistically in octahedral sites, whereas B cations alone are located in tetrahedral positions. There are also intermediate distributions which can be characterized by specifying the fraction of B ions on tetrahedral sites, $A_{1-x}B_x[A_xB_{2-x}]O_4$. The thermodynamically stable cation distribution in binary spinels depends on the values of the stabilization energy of octahedral and tetrahedral oxygen coordination for the different cations.

Several methods for synthesis of binary spinel products are usually applied:

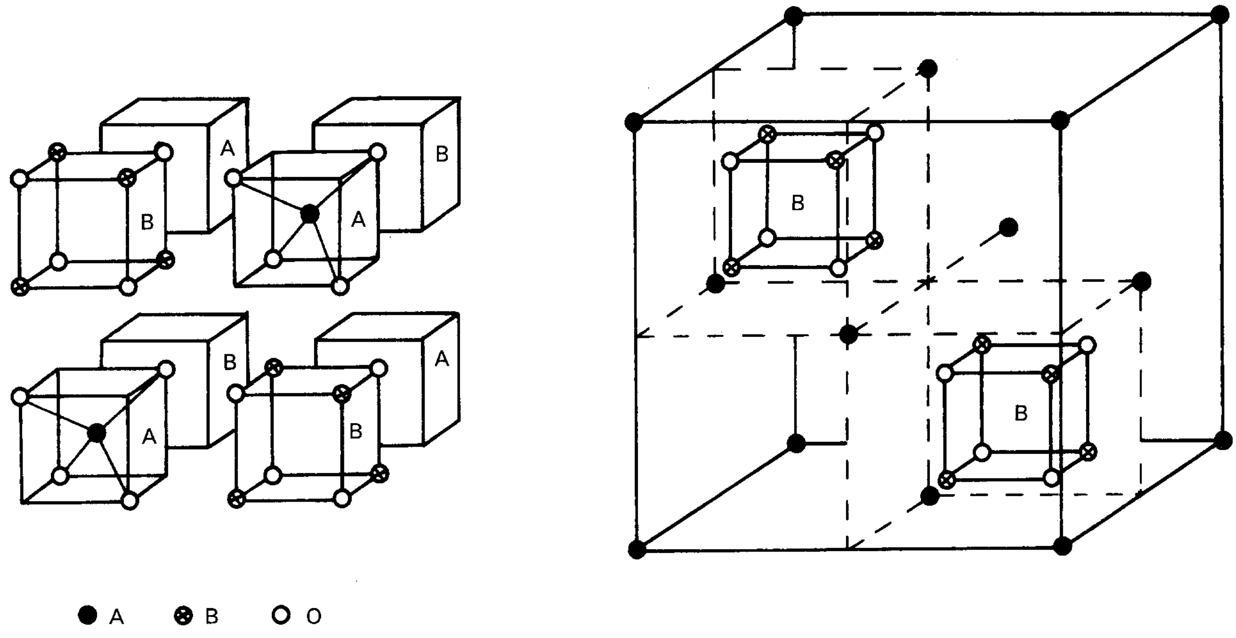

Figure 3 Idealized spinel structure. The lattice is built by alternating AO_4 and B_4O_4 units.

(i) a solid phase reaction between the metal oxides at high temperatures;

(ii) decomposition of mechanical mixtures of transition metal compounds;

(iii) coprecipitation of sparingly soluble compounds followed by thermal decomposition.

2. Synthesis of spinel cobaltites

2.1. Synthesis via solid-phase reaction between oxides

The limitations, associated with all solid phase reactions are valid in this case. The product formation reduces the area of contact between the reagents. The diffusion of the initial oxides through the product layer is a function of temperature, grain boundary contacts, the concentration of defects, etc. When an initial mixture of low surface area is used, the reaction proceeds to a smaller extent. A high surface area reaction mixture is much more favourable. For that reason, in many cases continuous grinding between heat cycles is employed.

In the process of spinel cobaltite formation by a solid-state reaction another restriction appears. The cobalt spinels, $Me_xCo_{3-x}O_4$ $(0 < x < 1,\ Me = \mathrm{Ni, Cu, Zn, Mg}$, etc.) are characterized by a limited temperature interval of stability. At temperatures in the range 1100–1200 K the spinel structure of cobaltites is no longer stable and a transformation to a rock salt structure takes place [39].

$$M_yCo_{3-y}O_4(\text{spinel}) \rightarrow M_zCo_{3-z}O_4(\text{spinel}) + MO + \underset{\text{rock salt}}{(M,Co)O} + O_2 \qquad (1)$$

It has been established by many authors [26–29] that even at lower temperatures, which depend on the nature of the divalent cation and the values of x, cobalt spinels decompose, evolving oxygen, to MeO and a spinel phase with a higher cobalt content.

$$M_xCo_{3-x}O_4(\text{spinel}) \rightarrow MO + M_yCo_{3-y}O_4(\text{spinel}) + O_2 \qquad (2)$$

The synthesis via solid phase reaction between oxides presupposes heating at temperatures of about 1000–1273 K, i.e. above the critical temperature of cobaltite stability (623–873 K). That is why some attempts to synthesize these cobaltites have proved unsuccessful and in the literature there have been contradictory opinions on the existence of copper cobaltite. Bertaut and Delorme [28], and more recently Delorme [29], obtained a mixture of two phases: CuO and a spinel with a lattice constant corresponding to Co_3O_4.

2.2. Synthesis from mechanical mixtures of transition metal compounds

Spinel synthesis by decomposition of mechanical mixtures of appropriate metal compounds, such as sulphates, nitrates, hydroxides, oxalates and carbonates, can be achieved at a lower temperature. The formation of the spinel structure is preceded by the decomposition of the chemical compounds or proceeds, in some cases, simultaneously with the thermolysis.

Depending on the process conditions and the nature of the cobalt compounds, the products of their thermal decomposition may be Co_3O_4, CoO or metallic Co. Co_3O_4 has a spinel structure that can be denoted as $CoCo_2O_4$ (cobalt cobaltite). It is formed when an excess of oxygen is ensured during the thermal decomposition of Co(II) nitrate [30], oxalate [2, 31], hydroxide [32, 33] or carbonate [34–36]. The final product in an inert atmosphere or *in vacuo* is CoO, while CoO and metallic cobalt are obtained from the oxalate.

Cobaltites of Zn, Ni and Cu were synthesized for the first time by Holgersson and Karlsson [37] in a very simple way: by evaporation of Co(II) and Me(II) nitrate solutions with a molar ratio $Co/Me = 2$ and calcination of the residue at 1073–1123 K. X-ray analysis showed a spinel structure of the final compound. More recently, copper–cobalt spinels were synthesized by decomposition of natural oxide minerals with the approximate composition $CuO \cdot Co_2O_3 \cdot H_2O$ at 473 K. The spinel lattice parameter varied over the range 8.04–8.11 Å [38]. The unsuccessful attempts of a number of authors to synthesize copper cobaltite questioned the existence of this compound [28, 29, 39, 40]. The studies of Rasines [40] confirmed the results obtained by Holgersson and Karlsson in 1929. The binary spinel obtained was, however, not single-phase. It contained products of the decomposition of cobaltites at high temperatures. The spinel lattice parameter as determined from the X-ray patterns was $a = 8.084$ Å – close to that of Co_3O_4.

Decomposition of nitrate salts at 623 K leads to the formation of copper cobaltite with a Cu content close to the stoichiometric with the formula $Cu_{0.9}Co_{2.1}O_4$ and a lattice parameter $a = 8.105$ Å. Nickel cobaltite has been synthesized by the same method from $Ni(NO_3)_4 \cdot 6H_2O$ and $3Co(OH)_2 \cdot 2CoCO_3 \cdot nH_2O$. The attempts of many authors to obtain stoichiometric copper cobaltite by the decomposition of mechanical mixtures of cobalt and copper compounds have led to no results. The synthesis temperatures used are lower than the critical temperature of cobaltite stability, but they do not suffice to activate bulk diffusion transport between the decomposition products. An inhomogeneous spinel phase, i.e. a mixture of $Cu_xCo_{3-x}O_4$ spinels with different x values have been obtained instead [45]. On the surface of copper cobaltite samples synthesized from nitrates an extremely high Cu/Co ratio of about two was evaluated by experiments with an electron microsonde. From the electronograms also a Cu_2CoO_3 phase was identified in the surface layer [42], which explains the failure in the synthesis of stoichiometric copper cobaltite.

2.3. Thermal treatment of coprecipitated products

The most promising methods for the synthesis of catalysts use thermolysis of suitable precursors, containing all the metal ions in a single phase. They are obtained mainly by coprecipitation of sparingly soluble compounds. The precipitation process is usually carried out by adding portions of the precipitating agent to a solution of *Me*(II) salts, taken in a stoichiometric ratio. If the solubility of the sparingly soluble compounds differ considerably, the precipitate is initially enriched in the component of lower solubility, whereas the amount of the higher solubility compound increases at the end of the process. After heating this inhomogeneous precipitate, a mixture of spinels with different compositions is obtained.

The preparation method may determine the morphology of the final product and the number and type of crystallographic phases. As low temperatures of preparation are usually preferred to preserve high surface areas, in most cases metastable products and cation distributions are obtained. The precursor should favour the production of a solid with high specific surface area, desired stoichiometry and number of phases, with optional interdispersion of these phases. In order to be used as precursors in the synthesis of mixed cobalt spinel oxides with preset properties, the coprecipitation products should meet several requirements [43], important among which are:

(i) phase homogeneity, which should be preserved during the thermal decomposition;

(ii) the ratio *Me*/Co in the precursor should correspond to the desired stoichiometry of the final product;

(iii) the mixed oxide should be obtained in a form where the active elements are in optimal states of oxidation/reduction and dispersion.

2.3.1. Coprecipitated hydroxides as precursors

Binary $Me_xCo_{3-x}O_4$ cobaltites (*Me* = Ni, Zn, Cu, Mn, Mg) have been synthesized by thermal treatment of mixed hydroxide crystals [24, 26] and the catalytic activity in toluene complete oxidation was studied [24]. As seen from Table II, large specific surfaces of the final products are obtained. Due to the restricted substitution of the copper ions in cobalt hydroxide, however, synthesis of a spinel with a maximum copper content has not succeeded.

2.3.2. The use of oxalates as precursors in the synthesis of spinel cobaltites

Cobalt(II) oxalate has been used as an initial reagent in the synthesis of Co_3O_4 spinel [2]. In a reducing or inert media the thermal dissociation proceeds to α-Co, β-Co or CoO. The decomposition in oxidation media is an exothermal process which permits the use of lower temperatures. Oxidation of Co and CoO to Co(III) is established in this case.

The synthesis of high dispersity cobaltites of Mg, Ni and Zn from oxalates has been reported [44]. The authors have established that coprecipitated oxalates dihydrates of composition $Me_{0.33}Co_{0.67}C_2O_4 \cdot 2H_2O$ (*Me* = Ni, Mg, Zn) form continuous solid solutions. The binary oxalates decomposed at low temperatures, the process being highly exothermal. DTA analysis showed that the oxidation Co(II) → Co(III) occurs after dehydration and before the decomposition. As mentioned already, in an inert atmosphere or *in vacuo* a pure spinel product cannot be obtained from oxalates. A *Me*O phase and elementary Co were found as by-products. To reduce the local overheating during the thermal decomposition, a thin oxalate layer was deposited on a porous glass frit and an air flow at a rate of $0.5\,l\,min^{-1}$ was passed through. This also ensures an oxidation medium. As a result, after heating at 523 K for 4 h single phase spinels were obtained.

TABLE II Specific surface area (in $m^2\,g^{-1}$) of the cobaltites, obtained from different initial compounds, measured by BET physisorption [26, 44, 45, 49–52, 57–59]

Synthesis from	Binary cobaltites of						
	Ni	Zn	Mn	Cu	Mg	Ca	Fe
Nitrate salts mixture	12	9	14	6		25	
Hydroxides	46	71		81	87		
Hydroxidenitrates	77	41		53	48		
Oxalates	94	82			63		
Hydroxide-carbonates	95	120		116			95
Complex compounds	12.4	65	24		47		116

Copper cobalt spinels synthesized from oxalates were studied as catalysts in propene oxidation to acrolein. In the samples of $Cu_xCo_{3-x}O_4$, with $x > 0.72$, a CuO phase was present. The cation distribution for samples of different compositions was investigated. For $x < 0.30$ the spinels were normal and Cu was found only on tetrahedral positions. For $x > 0.30$ the spinels were partly inverse. The highest selectivity in acrolein synthesis was established for the $Cu_{0.24}Co_{2.76}O_4$ composition [25].

2.3.3. Synthesis of binary cobaltites from mixed hydroxidenitrate crystals

Mixed hydroxidenitrate crystals with a layered type structure have proved promising for the synthesis of binary cobaltites [45]. It is established that they decompose in one step at temperatures below the critical temperature for existence of the spinel phase. The process is not accompanied by diffusion, but a collapse of the lattice is observed. By such a mechanism of oxide phase formation only a negligible part of the building units migrate short distances, which is energetically more favourable than transfer via solid-phase diffusion. The process of spinel phase formation is topotactic. According to Lotgering [47], the solid products obtained as a result of chemical reaction or solid-phase transformation proceeding by a topotactic mechanism have the same (or some equivalent) crystallographic orientations as the crystals of the initial salts.

In cases where the solubility of the elements of coprecipitation differ significantly, a reverse coprecipitation procedure is recommended [41]. For obtaining the hydroxidenitrates, the sodium base is added to nitrate solutions of *Me*(II) and Co(II) ions. The concentration of metal ions forming the lower-solubility hydroxidenitrate is maintained constant during the precipitation process and lower than that of the hydroxyl ions in the solution. Under these conditions, *Me*(II) and Co(II) in a constant ratio are coprecipitated at any moment. The conditions suitable for the process may be determined from the experimental data on the concentration and temperature range of formation of the hydroxidenitrates of the different metal ions. The synthesis of the hydroxidenitrates and the corresponding spinel phases by this method proceeds under non-equilibrium conditions [45].

Spinel cobaltites of Ni, Zn and Mg and a metastable phase of stoichiometric copper cobaltite have been synthesized from mixed hydroxidenitrate crystals. The possibility of obtaining zinc cobaltite with variations in the cationic distribution is also shown, using the ability of two-layer hydroxidenitrates to exchange their tetrahedrally coordinated cations from the intermediate layers with the *Me*(II) of the liquid phase after coming in contact with aqueous solutions of other divalent metal salts. Among the hydroxidenitrates which play the role of precursors, and the spinel oxides obtained from them, there is a genetic correlation. Single-phase products are obtained with a *Me*/Co molar ratio of 0–0.5, the distribution of ions in the cationic lattice of the corresponding hydroxidenitrate being preserved in the spinels, obtained, however, as metastable phases. The presence of structural defects is determined by the similarity between the cationic sublattices in the initial salt and the oxide product.

2.3.4. Synthesis of binary cobaltites from coprecipitated hydroxidecarbonates

Hydroxidecarbonates are often employed as precursors in the synthesis of binary oxide catalysts. The reduction of copper cobalt mixed oxides, obtained by thermal decomposition of coprecipitated hydroxidecarbonates, led to an active catalyst for hydrogenation of CO_2 [48]. Amorphous hydroxidecarbonate precursors were used in the synthesis of zinc cobaltite $Zn_xCo_{3-x}O_4$ and nickel cobaltite $Ni_xCo_{3-x}O_4$ with x values in the range 0–1 [49, 50], and copper cobaltite $Cu_xCo_{3-x}O_4$ with x varying in the interval 0–0.9 [51]. Although the products of coprecipitation are X-ray amorphous, the i.r. spectra of the precursor hydroxide carbonates characterize them as compounds with different short-range order from the mechanical mixture of the corresponding hydroxidecarbonates. Iron–cobalt spinel mixed oxides with $0.33 \leqslant$ $Fe/Co \leqslant 2$ and cationic vacancies on octahedral sites for samples with high iron content were synthesized from pyroaurite-like hydroxidecarbonates $[Co(II)_{1-x}Fe(III)_x(OH)_2]\,[Co_3]_{x/2} \cdot mH_2O$ [52]. The thermal decomposition of the precursor occurs at a temperature below 573 K and cobaltites with high specific surface areas are obtained (Table II). Mean particle sizes below 10 nm were determined from the transmission microscope images for these spinels. These compounds are important for their catalytic properties: zinc and nickel cobaltites show high activity in the complete oxidation of hydrocarbons while copper cobaltite is active in both CO oxidation and NO reduction [22, 24]. Reduction of the high-dispersity nickel cobaltite yields a very active bimetallic catalyst for CO and CO_2 methanation, no carbon deposition or carbide formation being detected [46]. Zinc cobaltite possesses the highest thermal stability, followed by nickel cobaltite, with respect to the reaction of phase segregation (Equation 2) [56]. Copper cobaltite is of considerably lower thermal stability, compared with other binary cobaltites. Above 623–673 K, copper oxide admixture is present, irrespective of the preparation method [45, 56]. Above 1200 K all cobaltites undergo phase transformation to a rock salt structure according to Reaction 1.

The surface oxygen plays an important role in oxidation/reduction reactions, where these compounds may be used as catalysts. The temperature programmed desorption (TPD) of oxygen allows the different forms of non-stoichiometric oxygen on the surface to be detected. The TPD spectrum of zinc cobaltite synthesized from coprecipitated hydroxidecarbonate shows a broad band of oxygen desorption in the range 573–673 K [49]. Comparison with the data on copper cobaltite [51] indicates a stronger bonding of the surface oxygen in $ZnCo_2O_4$. For both compounds the temperature range of oxygen desorption coincides with the interval within which these catalysts work [1, 12, 22–24].

By temperature programmed reduction (TPR) with hydrogen the oxygen forms with different reactivity can be distinguished. The TPR spectrum of zinc cobaltite reveals two peaks with maxima at 598 K and 673 K and a shoulder at 695 K (Fig. 4). They are attributed to the consecutive stepwise reduction Co(III) → Co(II), Co(II) → Co and Zn(II) → Zn. The first two peaks are in agreement with those reported for spinel Co_3O_4 [74]. For copper cobaltite a single intensive peak is registered with a maximum at 578 K and a small shoulder at 423 K, the latter possibly being due to weakly bound surface oxygen (Fig. 4b) [49, 51]. The ability of easily reducible cations (copper, silver) to promote reduction of cobalt and nickel oxides at lower temperature is known and is explained by the high rate of atom or cluster formation, that act further as centres for the reduction of cobalt oxides [60]. In the case of nickel cobaltite, with TPR peak maxima at 530 K, 588 K and 640 K, (Fig. 4c), the reduction steps follow the sequence Ni(II) → Ni, Co(III) → Co(II) and Co(II) → Co [50].

2.3.5. Multicomponent spinel cobaltites, obtained from hydroxidecarbonates

Coprecipitated hydroxidecarbonates have been employed successfully in the synthesis of various types of oxide catalysts [49–55, 61–64]. There are a large number of investigations on hydrotalcite-like phases as precursors of catalysts for CO hydrogenation, containing Cu, Zn, Co, Ni and Al (or Cr) [65–72], and the role of the preparation method in modifying the

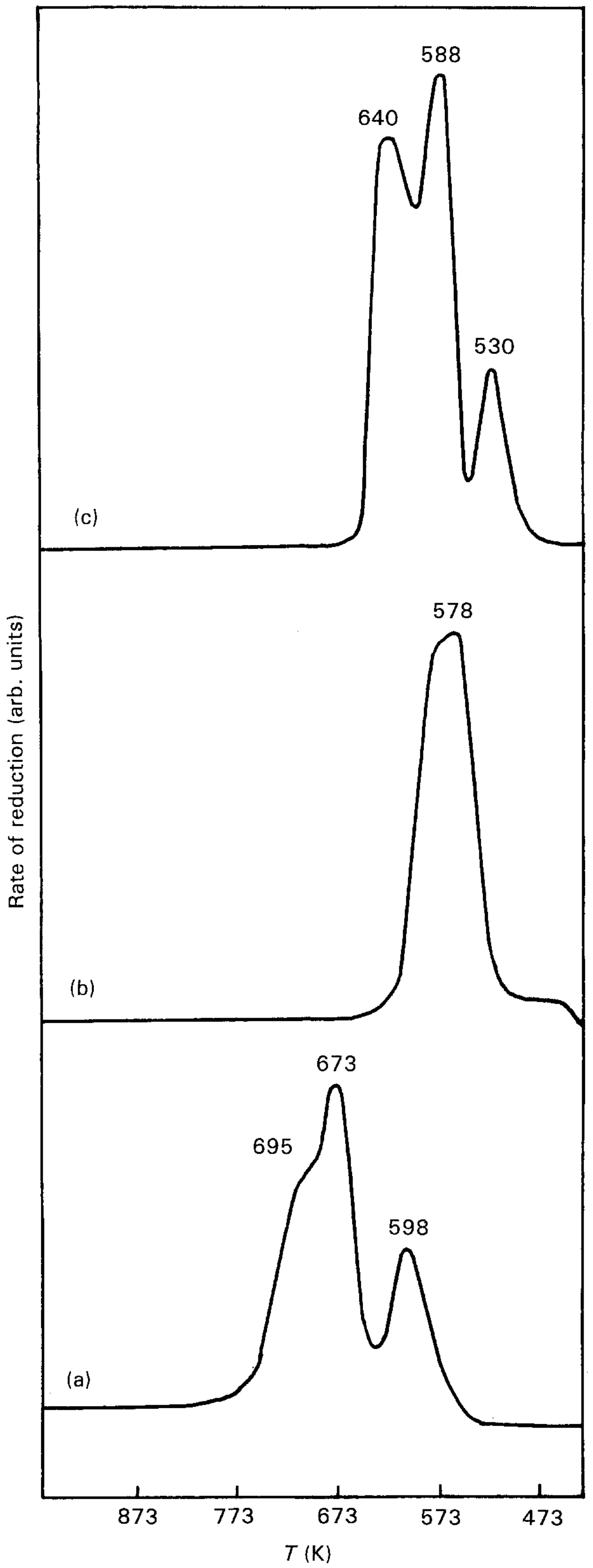

Figure 4 TPR profiles of transition metal cobaltites. Heating rate 25 K min^{-1}. (a) $ZnCo_2O_4$; (b) $Cu_{0.9}Co_{2.1}O_4$; (c) $NiCo_2O_4$.

acid–base properties of mixed oxides was emphasized [69–71].

The lattices of pyroaurite and hydrotalcite type $[Me(II)_{1-x}Me(III)_x(OH)_2]\,[CO_3]_{x/2}\cdot mH_2O$ are rather "hostile" and allow wide variations in composition. The kind and ratio of metal cations may be altered; more than two different cations can be introduced. Since they are statistically distributed among the octahedral positions of the cationic layers, a final oxide product with good interdispersion of the components is obtained.

Catalysts for the low temperature methanol synthesis consist generally of a Cu–Zn–Al(Cr) mixed oxide phase. The addition of cobalt in the ternary Cu–Zn–Al hydrotalcite-like phases leads to the formation of a homogeneous highly crystalline precursor with a lamellar structure. After thermal treatment at 620–670 K a spinel mixed oxide with high specific surface area (150–200 m^2 g^{-1}) is produced [43, 53].

A Cu/Co/Cr(Al, K) catalyst for selective C_1–C_6 alcohol synthesis in a reaction of CO hydrogenation was obtained by the use of coprecipitated hydroxide-carbonate precursor. Each step of the preparation procedure and the influence of the preparation conditions on the final selectivity towards C_1–C_6 alcohols were examined [53]. The effect of the composition of the catalyst was also discussed. Small amounts of Co yield very active and selective catalysts for this reaction, while the Co-rich samples are more effective as Fischer–Tropsch catalysts [48, 54, 73]. Cobalt mixed spinels with different compositions, containing Cu, Zn and Cr [54], have been investigated as catalysts in the Fisher–Tropsch synthesis of hydrocarbons. Depending on the relative ratios of Cu, Co, Zn and Cr, quasi-amorphous or crystalline hydrotalcite-like phases were obtained after coprecipitation with alkali carbonate from nitrate solutions at constant pH. Only in the samples with highest copper content, greater than 50%, was a malachite phase also present. After calcination, high-dispersity spinel mixed oxides with surface areas up to 90 m^2 g^{-1} were obtained. In order to explain the high catalytic activity of the samples, a synergic effect between the components was proposed.

2.4. Synthesis of cobaltites by a mechanochemical treatment

The mechanochemical method of synthesizing spinel products from the oxide components is relatively new and not well known. By scanning electron microsonde and other methods it was established that on the surface of $Cu_xCo_{3-x}O_4$ samples obtained by decomposition of nitrate mixtures the copper/cobalt ratio is almost twice as high as is its mean value for the sample [42], i.e. copper ions tend to concentrate mainly on the surface [42]. Hence, the surface layer of Co_3O_4 can "accept" definite amounts of copper. Mechanochemical treatment of a mixture of copper oxide and Co_3O_4 has led to the formation of copper-enriched surface layer of Co_3O_4 with a Cu/Co ratio of 1.

The fact that with the mechanochemical method the chemical interaction may proceed at room temperature is considered an advantage of this method. It is assumed that this is achieved as a result of a local increase in temperature (up to 10^3 K) and pressure (up to 10^8 Pa) in the regions of microcontact of the reagents, the mean temperature of the sample remaining unchanged. In these zones, melting (the so-called "magma–plasma" effect) may occur, which facilitates mutual penetration of the oxide components.

The mechanochemical synthesis of copper cobaltite can be realized by mixing copper oxide and Co_3O_4 in a 0.2:1 molar ratio and ultrasonic homogenization in an alcoholic suspension [42]. After drying, the product was subjected to mechanochemical treatment in a friction mill. The completion of the chemical reaction was judged by the absence of the most intense line of CuO from the X-ray patterns and the surface layer of copper cobaltite was examined by high-resolution electron microscopy (HREM) [75]. It was established that after heating at 623 K the mechanochemically obtained product decomposes to the initial phases (CuO and Co_3O_4).

Having in mind that copper cobaltite with a high copper content per formula unit is a metastable compound, it may be expected that it is mechanochemically reactive. After 10 h of grinding bulk copper cobaltite of composition $Cu_{0.76}Co_{2.24}O_4$ undergoes a phase segregation reaction of the type in Equation 1. A sample of lower copper content was chosen to avoid even minimum admixtures of copper oxide in the initial compound. Surface species containing Cu^+ were also detected in the XPS spectra of the mechanochemically treated cobaltite [76].

2.5. The use of complex compounds as precursors in the synthesis of fine-particle cobaltites

A new method of low temperature synthesis of cobaltites is reported in [57–59]. Complex compounds such as hydrazine carboxylate hydrates, $N_2H_5M_{1/3}Co_{2/3}(N_2H_3COO)_3 \cdot H_2O$ (where M = Mg, Mn, Fe, Co, Ni or Zn), metal acetate hydrazines $M_{1/3}Co_{2/3}(CH_3COO)_2(N_2H_4)_2$ (M = Ni and Zn) and *Me* oxalate hydrazinates (*Me* = Ni, Mg) have been investigated as precursors of spinel cobaltites. Coprecipitation and crystallization in solution were used for preparing the precursors. Their thermal dissociation at temperatures below 523 K leads to stoichiometric cobaltites consisting of fine particles with sizes of 1–40 μm and having specific surface areas of 12–115 $m^2 g^{-1}$ (Table II). Using complex compounds as precursors, the desired stoichiometry and a low impurity content are attained.

2.6. Synthesis of binary cobaltites on a support

High-dispersity cobaltites are obtained as fine powdery substances and have no mechanical stability. Their application as combustion catalysts requires better mechanical properties. The support should also stabilize the cobaltite phase on the surface. Alumina and ceramic materials are commonly used as supports of transition metal mixed oxides. An important problem arises with cobalt-containing oxides, because of their interaction with alumina, leading to the formation of an inactive cobalt aluminate phase [23, 77]. A new method for preparation of zinc cobaltite supported on granulated γ-alumina has been proposed by us [78], so that penetration of cobalt inside the grains is restricted to a minimum. High-dispersity zinc cobaltite is prepared by thermal decomposition of hydroxidecarbonate precursor and deposited on the support by employing dimethylformamide as a glue. In that way a stable and active combustion catalyst for organic substances (tested for acetone, toluene and styrene vapours) is obtained. The effectiveness of the catalyst (> 99.5% conversion to carbon dioxide and water) is also preserved in a wide concentration range – up to 3.0 $g m^{-3}$ for toluene, 2.5 $g m^{-3}$ for acetone and 1.5 $g m^{-3}$ for styrene.

3. Conclusion

On the basis of the present review, comparison of the different methods of cobaltite synthesis can be made. The qualities of the cobaltites obtained by these methods differ significantly. Their main applications as electrode materials and oxidation catalysts require high dispersity, homogeneity and lack of impurities in the spinel products. The solid-phase reaction between oxides at a high temperature leads to the formation of non-homogeneous products with a small specific surface area, which means that this reaction is not suitable for the synthesis. Besides, in some cases the temperature of synthesis is higher than the critical temperature of stability of the cobaltites, as a result of which additional phases appear. A little better results are achieved by decomposing mechanical mixtures of nitrates: the specific surface areas of the cobaltites are in this case of the order of 10 $m^2 g^{-1}$.

The mechanochemical synthesis is of definite interest, but some of the conditions of the reaction are not yet determined. In addition, the surface product obtained in this case has proved thermally unstable. Mechanochemically synthesized copper cobaltite begins to decompse at 623 K, while most of the catalytic processes are carried out at temperatures near to 623 K.

Cobaltite synthesis from precursors, usually obtained by coprecipitation, deserves special interest. The compounds appropriate for this synthesis are oxalates, hydroxysalts, hydroxides, some complex compounds, etc. For the preparation of a spinel product from oxalates, an oxidation medium during the thermal decomposition is needed. The use of complex compounds is very promising, but it should be mentioned that in some cases (e.g. $NiCo_2O_4$) very low specific surface areas are obtained. Coprecipitated hydroxides and basic salts may be used successfully in the synthesis of binary cobaltites. Among all basic salts hydroxidecarbonates prove to be the most perspective, as mixed oxides of high-dispersity are obtained, evolution of unpleasant or toxic gases is avoided during the thermal decomposition step and the desired stoichiometry, homogeneity and lack of impurities are achieved.

References

1. G. BORESKOV, V. POPOVSKII and V. SAZONOV, in Proceedings of the IVth International Congress on Catalysis, Moscow, 1970, edited by T. Eidus, V. Vassenberg, S. Kipperman, A. Rubinstein, B. Polkovnikov and T. Vinikov (Nauka, Moscow, 1970) Vol. 1, p. 343.

2. D. G. KLISSURSKI, *Commun. Chem. Bulg. Acad. Sci.* **8** (1961) 153.
3. *Idem., Int. Chem. Engng* **5** (1965) 19.
4. *Idem., C.R. Acad. Bulg. Sci.* **19** (1966) 297.
5. D. G. KLISSURSKI, T. POPOVA, N. ABADJIEVA and D. MILANOVA, *Chimia Industria* **57** (1970) 293.
6. D. G. KLISSURSKI, in Proceedings of the 3rd International Congress of the Iranian Chemical Society, Shiraz, 1975, edited by M. Behforouz, H. Khoshkhoo, S. Anderson, (Shiraz) p. 254.
7. D. DIMITROV, D. G. KLISSURSKI, Z. BULGARANOVA and L. FILIPOV, *Commun. Chem. Bulg. Acad. Sci.* **16** (1983) 164.
8. D. G. KLISSURSKI, in Proceedings of the 5th Iberoamerican Symposium on Catalysis, Plenary Lectures, Lisbon, 1976 (Quimica, Lisbon, 1979) Vol. 1, p. 29.
9. D. DIMITROV, D. G. KLISSURSKI, L. FILIPOV and Z. BULGARANOVA, *Chimia Industria* **56** (1981) 390.
10. D. G. KLISSURSKI, in Proceedings of the 4th International Congress on Catalysis, Moscow, 1968 (Ed. Acad. Kiado, Budapest, 1971) Vol. 1, p. 474.
11. D. G. KLISSURSKI, Z. BULGARANOVA and D. DIMITROV, in Heterogeneous Catalysis, Proceedings of the Vth International Symposium, Varna 1983, edited by D. Shopov, A. Andreev, A. Palazov and L. Petrov (Ed. BAS, Sofia, 1983) Part 1, p. 189.
12. T. ANDRUCHKEVICH, G. BORESKOV, V. POPOVSKII, V. MUZIKANTOV, O. KIMHAI and V. SAZONOV, *Kinet. Katal.* **9** (1968) 595.
13. T. ANDRUCHKEVICH, V. POPOVSKII and G. BORESKOV, *ibid.* **6** (1965) 860.
14. A. CRUCQ and A. FRENNET, in "Studies in surface science and catalysis, Vol. 30, Catalysis and automotive pollution control" (Elsevier, Amsterdam, 1987).
15. M. R. TARASEVICH and B. N. EFFREMEV, in "Electrodes of conductive metallic oxides", edited by S. Trasatti (Elsevier, Amsterdam, 1980) p. 221.
16. D. M. SHUB, A. N. CHEMODANOV and V. V. SHALAGINOV, *Elektrokhimia* **14** (1978) 595.
17. I. D. BELOVA, U. D. ROGINSKAYA, V. V. SHALAGINOV and D. M. SHUB, *J. Fiz. Khimii* **54** (1980) 1789.
18. H. M. CARAPUCA, M. PEPEIRA and F. DA COSTA, *Port. Electrochim. Acta* **7** (1989) 11.
19. J. SINGER and W. FIELDER, *J. Power Sources* **29** (1990) 443.
20. A. DAGHETTI and G. LODI, *Mater. Chem. Phys.* **8** (1983) 13.
21. S. TRASATTI, *J. Electroanal. Chem.* **111** (1980) 125.
22. G. GOLODETZ in "Studies in surface science and catalysis, Vol. 15, Heterogeneous catalytic reactions invovling molecular oxygen" (Elsevier, Amsterdam, 1983).
23. E. GARBOWSKI, M. GUENIN, M. C. MARION, M.PRIMET, *Appl. Catal.* **64** (1990) 209.
24. K. PAPADATOS and K. A. SHELSTAD, *J. Catal.* **28** (1973) 116.
25. H. BAUSSART, R. DELOBEL, M. Le BRAS and J. M. LEROY, *J. Chem. Soc. Faraday Trans. I* **75** (1979) 1337.
26. T. ANDRUSHKEVICH, G. BORESKOV, V. POPOVSKII, L. PLIASOVA, L. KARAKCHIEV and A. OSTANKOVITCH, *Kinet. Katal.* **9** (1968) 1244.
27. H. BAUSSART, M. Le BRAS and J. -M. LEROY, *C.R. Acad. Sci. Paris* **284** (1977) C-735.
28. F. BERTAUT and C. DELORME, *ibid.* **238** (1954) 1829.
29. C. DELORME. *Bull. Soc. Franc. Miner. Crist.* **81** (1958) 19.
30. D. WEIGEL, B. IMELIK and M. PRETTRE, *Bull. Soc. Chim. France* **836** (1964) 260.
31. G. PERINET, Le VAN MY and P. BIANCO, *C.R. Acad. Sci. Paris Ser. C* **266** (1968) 1152.
32. L. AVRAMOV, *Thermochim. Acta* **19** (1977) 147.
33. J. RICHARDSON and L. VERNON, *J. Phys. Chem.* **62** (1958) 1154.
34. A. BIELANSKI, K. DYREK, S. NIZIL and T. ROMANOVSKA, *Bull. Acad. Polon. Sci. Sci. Chim.* **15** (1967) 1603.
35. L. AVRAMOV and CHR. BETSCHEV. *Z. Anorg. Allg. Chem.* **383** (1971) 96.
36. H. HAGIHARA and E. ESHIGOYA, *Bull. Chem. Soc. Jpn* **38** (1965) 2163.
37. S. HOLGERSSON and A. KARLSSON, *Z. Anorg. Allg. Chem.* **183** (1929) 384.
38. V. BILLIET and A. VANDENDRIESSCHE, *Natuurwetensch. Tijdschr. Ghent* **21** (1940) 311.
39. F. DRIESSENS, G. RIECK and H. COENEN, *J. Inorg. Nucl. Chem.* **30** (1968) 747.
40. I. RASINES, *J. Appl. Cryst.* **5** (1972) 11.
41. H. H. KUNG, in "Studies in surface science and catalysis, Vol. 45, Transition metal oxides: surface chemistry and catalysis" (Elsevier, Amsterdam, 1989).
42. R. BONTCHEV, PhD. thesis, Sofia (1990).
43. PH. COURTY and CH. MARCILLY, in "Studies in surface science and catalysis, Vol. 16, Preparation of catalysts III", edited by G. Poncelet, P. Grange, P. Jacobs (Elsevier, Amsterdam, 1983) p. 485.
44. P. PESHEV, A. TOSHEV and G. GYUROV, *Mater. Res. Bull.* **24** (1989) 33.
45. L. MARKOV, PhD thesis, Sofia (1986).
46. D. G. KLISSURSKI, E. L. UZUNOVA and K. IVANOV, *Catal. Lett.* **15** (1992) 385.
47. F. K. LOTGERING, *J. Inorg. Nucl. Chem.* **9** (1959) 113.
48. H. BAUSSART, R. DELOBEL, M. Le BRAS and J. M. LEROY, *J. Chem. Soc. Faraday Trans. I* **83** (1987) 1711.
49. D. G. KLISSURSKI and E. L. UZUNOVA, *J. Mater. Sci. Lett.* **9** (1990) 576.
50. *Idem., Chem. Mater.* **3** (1991) 1060.
51. *Idem., J. Mater. Sci Lett.* **9** (1990) 1255.
52. E. L. UZUNOVA, D. G. KLISSURSKI, I. G. MITOV and P. C. STEFANOV, *Chem. Mater.* **5** (1993) 576.
53. PH. COURTY, D. DURAND, ED. FREUND and A. SUGIER, *J. Mol. Catalysis* **17** (1982) 241.
54. G. FORNASARI, S. GUSI, F. TRIFIRO and A. VACCARI, *Ind. Chem. Engng Res* **26** (1987) 1500.
55. J. NUNAN, P. HIMELFARB, R. HERMAN, K. KLIER, CH. BOGDAN and G. SIMMONS, *Inorg. Chem.* **28** (1989) 3868.
56. D. G. KLISSURSKI and E. L. UZUNOVA, *Thermochim. Acta* **189** (1991) 143.
57. K. C. PATIL, D. GAJPATHY and V. PAI VERNEKER, *J. Mater. Sci. Lett.* **2** (1983) 272.
58. G. MAHESH and K. PATIL, *Reactivity Solids* **4** (1987) 117.
59. P. RAVINDRANATHAN, G. MAHESH and K. PATIL, *J. Solid State Chem.* **66** (1987) 20.
60. R. ANDERSON, in "Catalysis, Vol. 4, Hydrocarbon synthesis, hydrogenation and cyclization", edited by Paul Emmett (Reinhold Publishing Co., New York, 1956) p. 82.
61. P. PORTA, G. DEL FIERRO, M. LO JACONO and G. MORETTI, *Catal. Today* **2** (1988) 675.
62. P. PORTA, S. DE ROSSI, G. FERRARIS, M. LO JACONO, G. MINELLI and G. MORETTI, *J. Catal.* **109** (1988) 367.
63. P. PORTA, R. DRAGONE, G. DEL FIERRO, M. INVERSI, M. LO JACONO and G. MORETTI, *J. Mater. Chem* **1** (1991) 531.
64. P. PORTA, G. MORETTI, M. MUSICANTI and A. NARDELLA, *Catal. Today* **9** (1991) 211.
65. P. GHERARDI, O. RUGGERI, F. TRIFIRO, A. VACCARI, G. DEL PIERO, G. MANARA and B. NOTARI, in "Studies in surface science and catalysis, Vol. 16, Preparation of catalysts III", edited by G. Poncelet, P. Grange and P. Jacobs (Elsevier, Amsterdam, 1983) p. 723.
66. S. GUSI, F. PIZZOLI, F. TRIFIRO, A. VACCARI and G. DEL PIERO, in "Studies in surface science and catalysis, Vol. 31, Preparation of catalysts IV", edited by B. Delmon, P. Grange, P. Jacobs and G. Poncelet (Elsevier, Amsterdam, 1987) p. 753.
67. O. CLAUSE, M. GAZZANO, F. TRIFIRO, A. VACCARI and L. ZATORSKI, *Appl. Catal.* **73** (1991) 217.
68. O. CLAUSE, B. REBOURS, E. MERLEN, F. TRIFIRO and A. VACCARI, *J. Catal.* **133** (1991) 231.
69. G. BUSCA, V. LORENZELLI and V. ESCRIBANO, *Chem. Mater.* **4** (1992) 595.
70. G. BUSCA, V. LORENZELLI and V. BOLIS, *Mater. Chem. Phys.* **31** (1992) 221.

71. G. BUSCA, F. TRIFIRO and A. VACCARI, *Langmuir* **6** (1990) 1440.
72. F. CAVANI, F. TRIFIRO and A. VACCARI, *Catal. Today* **11** (1991) 173.
73. F. LIN and F. PENNELA, in "Catalytic conversions of synthesis gas and alcohols to chemicals", edited by R. Herman (Plenum Press, New York, 1984) p. 53.
74. S. BHATIA, J. BELTRAMINI and D. DO, *Catal. Today* **7** (1990) 360.
75. R. BONTCHEV, T. ZHELEVA and S. SEVOV, *Chem. Mater* **2** (1990) 93.
76. D. KLISSURSKI and E. UZUNOVA, *J. Mater. Chem.* **2** (1992) 653.
77. D. KLISSURSKI, E. UZUNOVA and K. YANKOVA, *Appl. Catal. A: General* **95** (1993) 103.
78. C. -S. BAI, S. SOLED, K. DWIGHT and A. WOLD, *J. Solid State Chem.* **91** (1991) 148.

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