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Influence of preparation method on catalytic properties of mixed calcium–cobalt orthophosphates

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Mixed calcium–cobalt orthophosphates of the formula $Ca_{3-x}CO_x(PO_4)_2$, with $0 \leqslant x \leqslant 1.1$, were prepared by coprecipitation and solid-state reaction. Structural characterization showed that, in both cases, the solids obtained resulted from substitution of some Ca^{2+} ions by Co^{2+} ions in the β-$Ca_3(PO_4)_2$ structure. The solubility limit of cobalt in this structure corresponded to $x = 0.31$. The morphology of these compounds was investigated by surface-area measurements and scanning electron microscopy. When tested in the 2-propanol decomposition reaction, the maximum activity in dehydrogenation was obtained with the compound corresponding to cobalt maximum solubility in β-$Ca_3(PO_4)_2$ structure. Higher activities were obtained for samples prepared by coprecipitation.

1. Introduction

Phosphates have stimulated considerable attention and continue to interest many investigators, both in practical and fundamental aspects, because of their chemical and physical properties [1]. They are used in numerous domains of heterogeneous catalysis [2].

Amongst bimetallic phosphates, the calcium–nickel industrial catalyst for olefin dehydrogenation is an important catalyst for obtaining the principal monomers of synthetic rubber, butadiene and isopropene [3]. This catalyst was subject to several studies [4–8].

This study investigates the behaviour of another transition metal "cobalt" engaged in the same matrix "tricalcium phosphate (TCaP)". It forms part of a wider study encompassing the preparation, characterization and catalytic testing of mixed orthophosphates corresponding to the formula $Ca_{3-x}M_x(PO_4)_2$ where M = Ni, Co, Zn and Cd. It addresses the problems related to the identification of the active components of the catalysts and the determination of their role, which requires a detailed study of their genesis, phase composition and texture.

We report here on the characterization and the catalytic properties of a series of mixed calcium–cobalt phosphates (CaCoP), prepared by two different procedures; namely, coprecipitation and solid-state reaction.

Structural characterization was done by infrared spectroscopy (IR) and X-ray diffraction (XRD). The morphological features of these compounds were investigated by gas adsorption and scanning electron microscopy (SEM).

The catalyst action was compared, for both series, with respect to the 2-propanol decomposition reaction using a continuous flow fixed-bed system.

2. Experimental procedure

2.1. Materials

Two series of the mixed phosphate catalysts were prepared by coprecipitation and solid-state reaction. The preparation method, physicochemical characterization, as well as the thermal behaviour of the catalysts prepared by coprecipitation, were reported in more detail elsewhere [9]. The 40–60 μm fraction of dried precipitates was activated by calcination at 850 °C for 2 h. For the solid-state reaction preparation, pure β-TCaP [10] and γ-tricobalt phosphate (γ-TCoP) [11] were first synthesized by coprecipitation and characterized by chemical analyses, XRD, IR, differential thermal analysis (DTA) and thermogravimetry (TG). Many samples covering the range $0 \leqslant x \leqslant 3$ were prepared by grinding of the mixtures for 30 min repeated five times before heating them at 850 °C for 24 h. The orthophosphate compositions were determined by chemical analyses for samples prepared by coprecipitation; they were deduced from the mixed amounts of the initial orthophosphates in

TABLE I Composition of $Ca_{3-x}Co_x(PO_4)_2$ catalysts prepared by coprecipitation (COP) and solid-state reaction (SSR)

x (COP)	0.04	0.08	0.11	0.17	0.20	0.24	0.27
	0.32	0.35	0.41	0.45	0.66	0.94	1.10
x (SSR)	0.10	0.20	0.25	0.30	0.40	0.50	0.60

the case of samples prepared by solid-state reaction. The compositions of the samples used in the course of this study are gathered in Table I.

2.2. Physicochemical characterization

IR absorption spectra were registered on a Perkin–Elmer 575 spectrophotometer from thin discs containing approximately 2 mg sample and 300 mg spectroscopic KBr.

The XRD equipment used consisted of a CGR Theta 60 X-ray generator. The powdered samples were rotated whilst being exposed to CoK_α radiation.

BET surface-area measurements were carried out on a Carlo Erba 1800 Sorptomatic by adsorption of nitrogen at liquid air temperature.

SEM was undertaken with a Jeol 25S3 instrument operated at 15 kV. Samples were mounted separately on aluminium stubs and precoated with gold in a sputter coater to minimize the severe charging effects that proved to be characteristic of these materials.

2.3. Catalytic tests

The catalytic studies of 2-propanol decomposition were performed in a continuous flow system at atmospheric pressure. The catalyst (50 mg), deposited on a sintered glass inside the reactor, was flushed continuously by a stream of nitrogen (27.4 ml min^{-1}) saturated with 2-propanol at 30 °C (partial pressure 58 torr; 1 torr = 133.322 Pa). The temperature of the reactor was regulated automatically at 350 °C. The analysis of the component gases was carried out by on-line gas chromatography, using a Hewlett–Packard 575 chromatograph equipped with a flame ionization detector. Resolution of reactant and reaction product mixtures was achieved using a stainless steel column packed with 15% Carbowax 1500 supported on NAW chromosorb.

The conversion rate, C, and the selectivity, S, for acetone were defined as: C, the amount of alcohol converted/initial amount of alcohol; and S the amount of acetone/amount of alcohol converted.

3. Results and discussion

3.1. Infrared spectroscopy

The IR spectra exhibited by the catalysts prepared by both methods correspond to that found for pure β-TCaP (Fig. 1), which was in agreement with spectra given in the literature for this compound [12, 13].

Typical for this spectrum are the bands at 1200–950 and 550–650 cm^{-1}, which are composed of several sharp peaks. All of these modes are relevant for PO_4^{3-} groups. The greater number of peaks in the mixed phosphate spectra can be understood because the substitution of Ca^{2+} ions by smaller Co^{2+} ions leads to distortions in the original structure of β-TCaP.

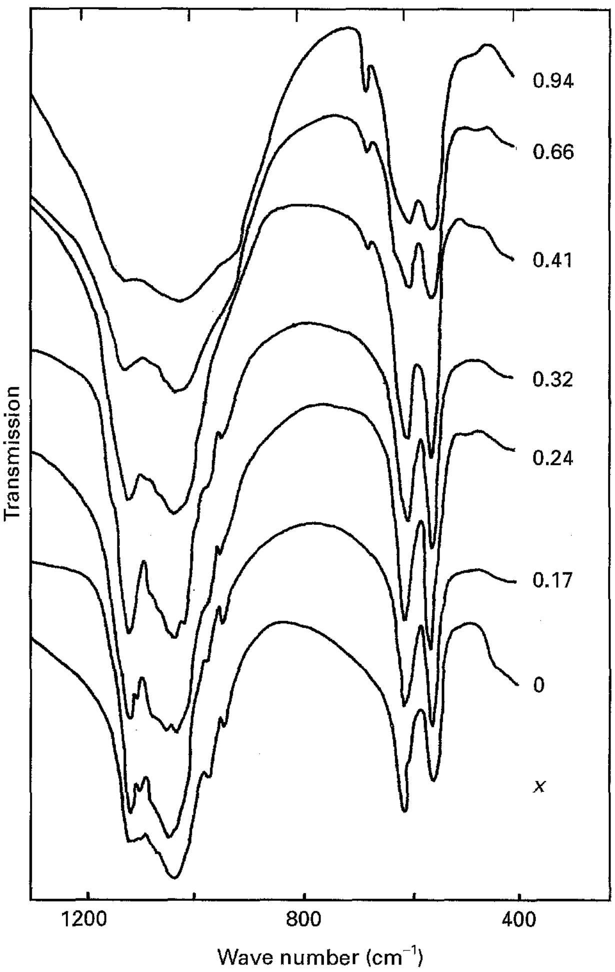


Figure 1 IR spectra for CaCoP catalysts compared to that of pure β-TCaP.

However, the catalysts prepared by coprecipitation presented, in addition, bands at 3600, 1600 and 1210 cm^{-1}, which indicate that the products contain traces of water. An additional band was present, in the spectra of samples for which $x \geqslant 0.40$, at 675 cm^{-1}. This band can be attributed to another phase which was identified by XRD to be of stanfeldite type.

It is noteworthy that absorptions corresponding to undesired pyrophosphate ions, $P_2O_7^{4-}$, [12, 14, 15] were absent from these spectra.

3.2. X-ray diffraction

Analysis of the XRD patterns of the catalysts prepared by coprecipitation and calcined at 850 °C, as well as those prepared by the solid-state reaction enabled their classification into two groups:

(i) $x \leqslant 0.32$ for coprecipitation and $x \leqslant 0.40$ for solid-state reaction;

(ii) $x > 0.32$ for coprecipitation and $x > 0.40$ for solid-state reaction.

The first group is constituted of single-phase solid solutions of β-TCaP [16, 17] in which some calcium ions had been replaced with cobalt ions. However, because the ionic radius of cobalt (0.072 nm) is smaller

TABLE II Comparison between d spacings ($I/I_0 \geqslant 20$) of stanfeldite and those of the phase obtained as a mixture with cobalt substituted β-TCaP in compounds with $x > 0.40$

Stanfeldite [20]		d (nm)		
d (nm)	I/I_0	$x = 0.66$	$x = 0.94$	$x = 1.10$
0.831	50			
0.601	50		0.6009	0.5996
0.500	30		0.5028	0.5013
0.384	60	0.3853	0.3854	0.3846
0.375	80	0.3749	0.3750	0.3744
0.325	30		0.3448	0.3265
0.304	30	0.3057	0.3057	0.3056
0.2817	100	0.2814	0.2813	0.2811
0.2734	20			
0.2695	30			0.2693
0.2505	80	0.2507	0.2509	0.2508

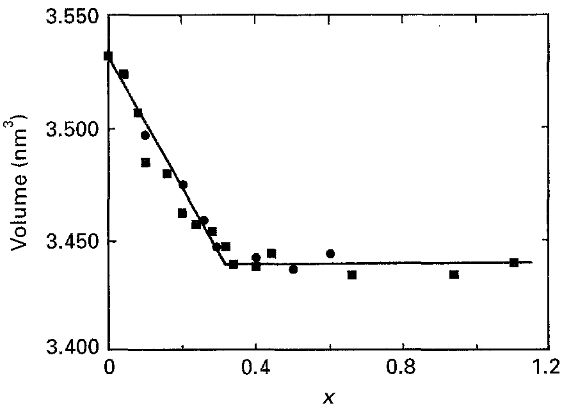


Figure 2 Unit cell volume evolution with cobalt content for the mixed CaCoP catalysts, $Ca_{3-x}Co_x(PO_4)_2$, prepared by (■) coprecipitation and (●) solid-state reaction.

than that of calcuim (0.099 nm), the rhombohedral lattice of TCaP is contracted.

In the second group, additional d spacings were observed inferring the presence of another crystalline component which was identified to be of stanfieldite type (Table II) [18–20]. The latter phase was isolated by us as pure in the range $1.6 \leqslant x \leqslant 1.70$ [18].

The cell parameters for all samples were refined with a least-squares computer program using the hexagonal setting of R3c. The evolution of the unit cell volume in relation with the amount of cobalt indicates that Vegard's law is obeyed (Fig. 2). The solubility limit of cobalt in the β-TCaP lattice was estimated at $x = 0.31$ for both series.

Taking into account experimental errors, this value is in agreement with that determined by Nord [21] and is compatible with the occupation of a certain type of sites in the structure of β-TCaP. In fact, β-TCaP contains five distinct calcium sites denoted $Ca^{(1)}$ to $Ca^{(5)}$ by Dickens *et al.* [17]. $Ca^{(4)}$ and $Ca^{(5)}$ sites which constitute 4.76% and 9.52% of the total calcium sites, respectively, are octahedral. The other three sites which constitute 28.57% each, have the following coordination numbers: $Ca^{(1)}$, 7, $Ca^{(2)}$, 8, and $Ca^{(3)}$, 8.

The Co^{2+} ion with its smaller radius tends to occupy preferentially octahedral sites and the site $Ca^{(5)}$ seems particularly favourable because of its shorter Ca–O bonds. This type of site has been observed to be occupied by magnesium in the whitlockite [22]. Meanwhile, a simultaneous occupation of neighbouring $Ca^{(4)}$ and $Ca^{(5)}$ sites can also be considered [23]. In both cases, the corresponding value for x is 0.29.

TABLE III BET surface area of CaCoP catalysts [$Ca_{3-x}Co_x(PO_4)_2$] prepared by coprecipitation and calcined at 850 °C

	x			
	0.08	0.17	0.27	0.32
S ($m^2 g^{-1}$)	10.5	10.0	9.5	9.5

3.3. Surface area

The BET surface-area measurements indicate that the catalysts prepared by coprecipitation have almost the same surface area of about 10 $m^2 g^{-1}$ whatever their cobalt content (Table III). Those prepared by solid-state reaction presented very low surface areas which could not be measured by the apparatus used in the course of this study. The difference between the two series can be explained by the sintering phenomenon, because the compounds prepared by solid-state reaction were subjected to a longer heating time (120 h).

3.4. Scanning electron microscopy

SEM observation of the samples revealed morphological similarities between all of them at low magnification. They consist of well-formed crystals with different shapes. Their sizes are within the desired granulometry of 40–60 μm.

At higher magnification (Fig. 3), they are seen to be constituted of agglomerated fine spherical particles. These particles are very small in the case of the samples prepared by coprecipitation. They are very much bigger in the case of those prepared by solid-state reaction, due to sintering. This confirms the observations made by BET surface-area measurements.

3.5. Catalytic tests

Preliminary tests showed that the activity of the catalysts increased with time and a steady state was reached after an induction period of about 4.5 h.

The activities and selectivities of different samples, measured after the steady state was reached (~5 h), are given in Fig. 4. Analysis of these curves shows that the activity increases rapidly and reaches a maximum when $x = 0.30$ and 0.28 for the catalysts prepared by coprecipitation and solid-state reaction, respectively. For higher x values the activity decreases drastically. This decrease might be due to the presence of the new phase, which was identified by XRD as of stanfeldite type. The maximum catalytic activity coincides with the solubility limit of cobalt in the structure of β-TCaP.

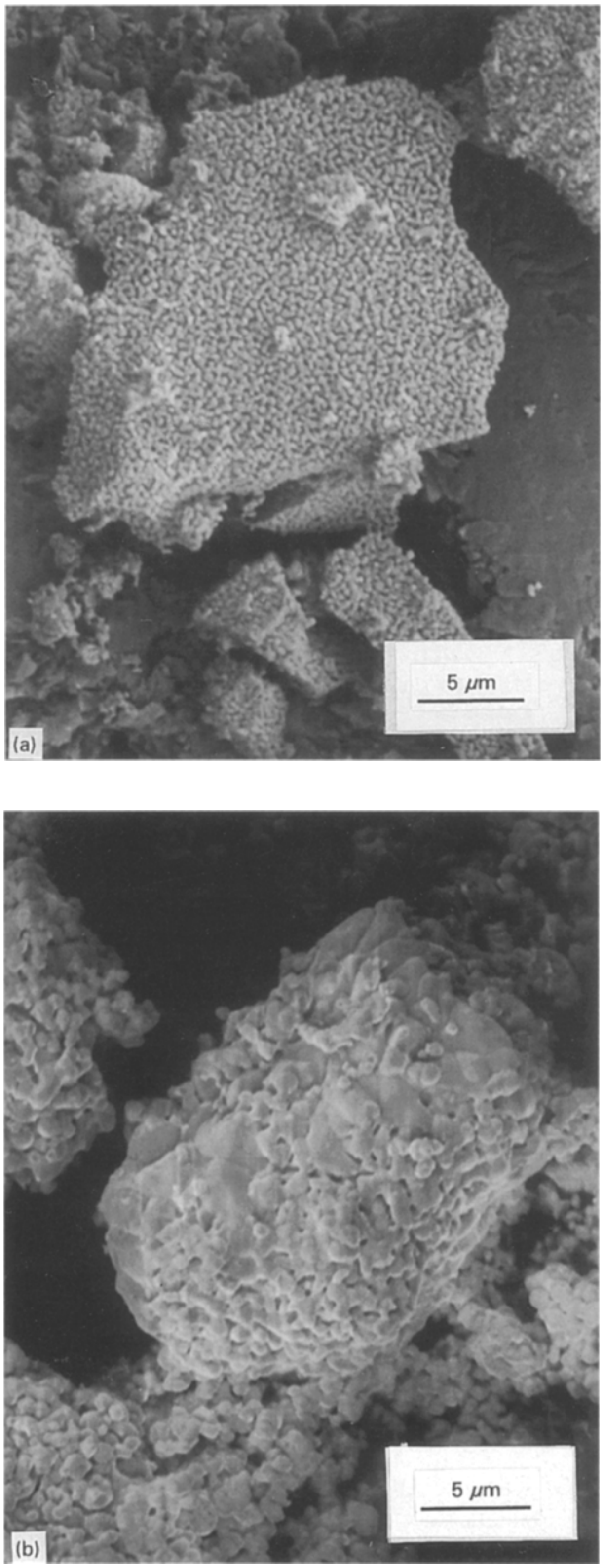


Figure 3 Scanning electon micrographs of CaCoP catalysts prepared by (a) coprecipitation and (b) solid-state reaction.

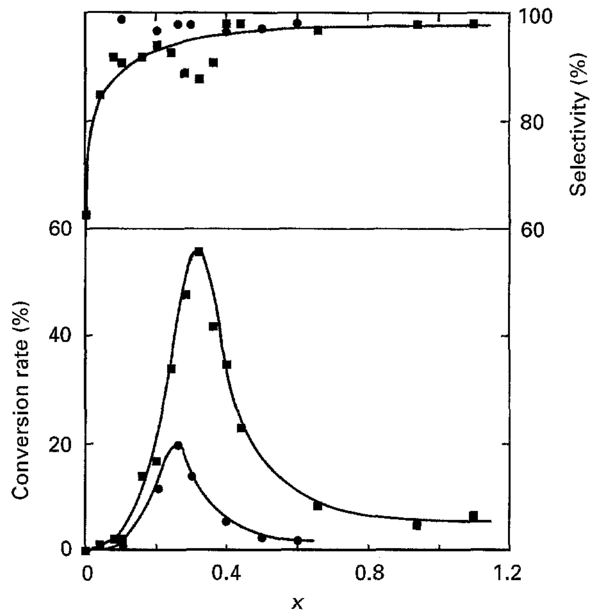


Figure 4 Conversion rate and selectivity for acetone of the CaCoP catalysts, $Ca_{3-x}Co_x(PO_4)_2$, prepared by (■) coprecipitation and (●) solid-state reaction.

The catalysts prepared by coprecipitation were more active than those prepared by solid-state reaction, in agreement with the morphological observations made by surface-area measurements and SEM. The higher selectivity obtained with samples prepared by solid-state reaction can be explained by their very low activity.

The structure–activity relation of these phosphates shows that the dehydrogenating activity is only obtained when the phosphate was crystalline with substitution of calcium by cobalt. In fact, when both pure β-TCaP and γ-TCoP were tested, they showed very low activity, mainly dehydrating.

The dehydrating activity observed for some samples with low cobalt content must be due to the presence of acidic sites at the surface of the catalyst. It might be that the transformation of HPO_4^{2-} into $P_2O_7^{4-}$ during calcination was not total or some water molecules were retained in the solid and dissociated at its surface. In this case cobalt does not play any role and the active sites are similar to those present in β-TCaP [24, 25], zinc phosphates [26] or hydroxyapatite [27–29].

Dehydrogenating activity can be attributed, as shown by electron spin resonance in the mixed Ca–Ni phosphates [7], to the formation of Co^{3+} ions during thermal activation of the CaCoP. These ions contribute in the following oxydo-reduction mechanism:

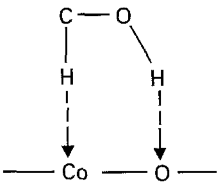
$$CH_3CHOHCH_3 \rightarrow CH_3COCH_3 + 2H^+ + 2e^- \quad (1)$$

$$2Co^{3+} + 2e^- \rightarrow 2Co^{2+} \quad (2)$$

$$2Co^{2+} + 2H^+ \rightarrow 2Co^{3+} + H_2 \quad (3)$$

However, once some hydrogen is formed from the reaction, and taking the cases where dehydrogenation dominates dehydration so that the hydrogen/steam ratio is high, then the reduction of cobalt cations to their metallic state, which is likely to have great dehydrogenating activity, appears possible.

Kinetics studies were carried out on the most active catalyst in the series prepared by coprecipitation [30]. It was noticed that phenol was strongly chemisorbed on basic sites of the catalyst which must be phosphate groups while pyridine was weakly chemisorbed on acidic sites which are cobalt atoms. Therefore, it was thought that both acidic and basic sites act simultaneously during dehydrogenation. Hence, a two site mechanism was adopted (I).



(I)

A similar mechanism was proposed for 2-propanol dehydrogenation on hydroxyapatite [25] and mixed Ca–Ni phosphate [7].

4. Conclusion

Mixed Ca–Co phosphate catalysts of formula $Ca_{3-x}Co_x(PO_4)_2$ were prepared by coprecipitation and solid-state reaction.

Their structural characterization, by IR and XRD, showed that solid solutions based on β-TCaP, with substitution of some Ca^{2+} ions by Co^{2+} are formed. The solubility limit of cobalt in β-TCaP structure corresponds to a value of x around 0.30, which coincides with the occupation of the octahedral sites.

The surface area of the catalysts prepared by coprecipitation was greater than that of samples prepared by solid-state reaction. Samples from both series were observed in the SEM as being constituted of agglomerated fine spherical particles. These particles are larger in the case of samples prepared by solid-state reaction, due to sintering. This shows the impact of the preparation procedure on the texture of these kinds of materials.

The catalytic tests indicated that it is cobalt substitution in β-TCaP structure which is responsible for their catalytic activity. The maximum activity in 2-propanol decomposition reaction was observed, for both series, to correspond to the limit of solubility of cobalt in β-TCaP.

As expected, the samples prepared by coprecipitation, which present a higher surface area, are more active catalysts.

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