

Synthesis, characterization and catalytic behaviour of $\text{Cu}_{0.5}\text{M}_2(\text{PO}_4)_3$ ($\text{M} \equiv \text{Zr, Sn, Ti}$)

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Abstract

Phosphates of the form $\text{Cu}_{0.5}\text{M}_2(\text{PO}_4)_3$ ($\text{M} \equiv \text{Zr, Sn, Ti}$) were prepared by the oxidation of $\text{Cu}^{\text{I}}\text{M}_2(\text{PO}_4)_3$ or by a sol-gel route. These compounds were characterized by X-ray diffraction, EPR and optical spectroscopy. In $\text{Cu}_{0.5}\text{Zr}_2(\text{PO}_4)_3$, temperature-programmed reduction measurements gave evidence of two types of sites for Cu^{2+} ions.

The catalytic behaviour of these phosphates in the decomposition of isopropyl alcohol seemed to operate mainly by a dehydration process related to the presence of hydroxyl and $(\text{HPO}_4)^{2-}$ groups on the surface of the samples, particularly on $\text{Cu}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ synthesized by the sol-gel method.

1. Introduction

The Nasicon-type structure consists of a three-dimensional skeleton made up of (MO_6) octahedra and (PO_4) tetrahedra sharing corners and delimiting interconnected tunnels, which explains the high mobility of M^+ ions in this material [1, 2].

Besides this remarkable conduction property, copper(I) zirconium phosphate shows interesting catalytic behaviour in the decomposition of alcohols. The main feature of this process is dehydrogenation (production of acetone or butanone). $\text{CuZr}_2(\text{PO}_4)_3$ also exhibits an aperiodic oscillatory activity related to Cu^+ diffusion as well as to its reduction to Cu^0 on the surface [3, 4].

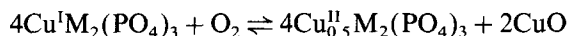
The basic structure framework $[\text{M}_2(\text{PO}_4)_3]^-$ is not destroyed in oxidation reactions [5]. In investigating its catalytic properties, it seemed worth while to study copper(II)-M(IV) phosphates ($\text{M} \equiv \text{Zr, Ti, Sn}$). Usually, copper(II)-containing solids (zeolites or phosphates) have excited interest because of their selectivity in reactions involving hydrogen.

This report is a description of the synthesis, structural and physicochemical investigations, and also catalytic properties of the compounds $\text{Cu}_{0.5}\text{M}_2(\text{PO}_4)_3$ ($\text{M} \equiv \text{Zr, Ti, Sn}$).

2. Preparation

Phosphates $\text{Cu}_{0.5}\text{M}_2(\text{PO}_4)_3$ ($\text{M} \equiv \text{Zr, Ti, Sn}$) were prepared by oxidation of $\text{Cu}^{\text{I}}\text{M}_2(\text{PO}_4)_3$ at about 450 °C

(method 1):



Above 500 °C, this reaction is partially reversible. CuO was removed by washing the reaction products with dilute HNO_3 .

To avoid CuO or $\text{Cu}_{1+x/2}\text{M}_2(\text{PO}_4)_3$ formation, but especially to obtain materials of high specific area ($\text{M} \equiv \text{Zr, Sn}$) a second method (referred to here as method 2) via a sol-gel route was preferred. The starting compounds $\text{ZrOCl}_2 \cdot \dots \cdot 8\text{H}_2\text{O}$ (or $\text{SnCl}_4 \cdot \dots \cdot 5\text{H}_2\text{O}$) and CuO were separately dissolved in water or 2N HNO_3 . The solutions were mixed in stoichiometric proportions. The addition of a solution of $(\text{NH}_4)_2\text{HPO}_4$ with constant stirring produced a gelatinous precipitate. The gel and the supporting solution were maintained at 80 °C for 24 h and then progressively heated at various temperatures between 500 and 800 °C to obtain different degrees of crystallinity.

TABLE 1. Surface areas of $\text{Cu}_{0.5}\text{M}_2(\text{PO}_4)_3$ samples

Composition	Preparation methods (1 or 2)	Calcined samples T (°C)	Surface area ($\text{m}^2 \text{g}^{-1}$)
$\text{Cu}_{0.5}\text{Ti}_2(\text{PO}_4)_3$	(1)	600	1.6
$\text{Cu}_{0.5}\text{Zr}_2(\text{PO}_4)_3$	(1)	600	7.6
$\text{Cu}_{0.5}\text{Sn}_2(\text{PO}_4)_3$	(1)	600	0.2
$\text{Cu}_{0.5}\text{Zr}_2(\text{PO}_4)_3$	(2)	500	93.3
$\text{Cu}_{0.5}\text{Zr}_2(\text{PO}_4)_3$	(2)	700	46.7
$\text{Cu}_{0.5}\text{Sn}_2(\text{PO}_4)_3$	(2)	600	9.6

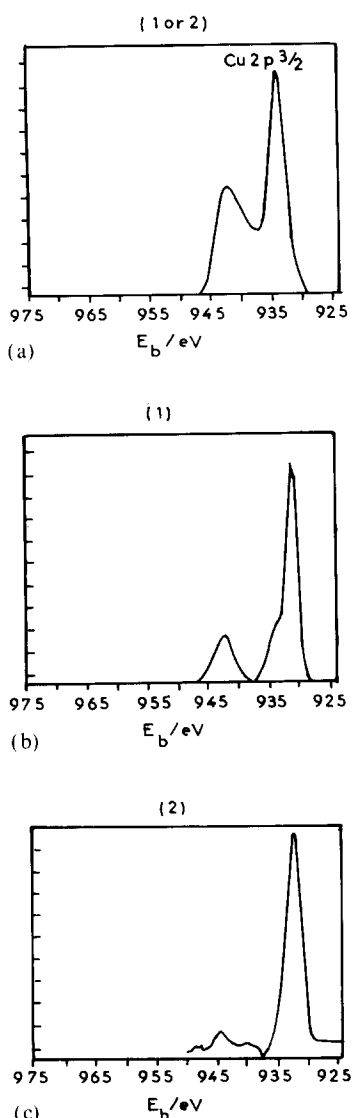


Fig. 1. X-ray photoelectron spectra of $\text{Cu}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ (a) made by methods 1 and 2, before the catalytic run; (b) made by method 1, after treatment with isopropyl alcohol at 240°C ; (c) made by method 2, after treatment with isopropyl alcohol at 240°C .

TABLE 2. Surface composition of $\text{Cu}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ (prepared by method 2)

Atomic ratio	Cu/Zr	Cu/P	Zr/P	O/P	O/Zr
Theoretical	0.25	0.16	0.66	4	6
Experimental	0.26	0.15	0.58	3.90	6.72

As expected, the specific areas as measured by the Brunauer–Emmett–Teller (BET) method were higher for sol–gel samples and reached $93\text{ m}^2\text{ g}^{-1}$ for $\text{Cu}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ (Table 1).

In addition, an X-ray photoelectron spectroscopy (XPS) study was carried out on this latter product (Fig. 1(a)). The major species corresponded to Cu^{2+} ions

(binding energy of $(2p)^{3/2} = 934.9\text{ eV}$ with a higher energy satellite peak at 943.4 eV). The surface composition was close to bulk theoretical values (Table 2).

3. Structural investigation

At room temperature (RT), the X-ray diffraction (XRD) powder patterns from $\text{Cu}_{0.5}\text{M}_2(\text{PO}_4)_3$ made by both methods showed a monoclinic distortion compared with the $\text{NaZr}_2(\text{PO}_4)_3$ structure ($R\bar{3}c$). Furthermore, but only when $\text{M} \equiv \text{Zr}$, two different XRD patterns were obtained depending on the synthesis method, as previously observed [6]. Samples prepared by the sol–gel route were presumed to be of the $\text{Sc}_2(\text{WO}_4)_3$ type. This latter structure is known to be closely related to the Nasicon structure [7]. Parameters of the Nasicon or $\text{Sc}_2(\text{WO}_4)_3$ monoclinic cell in these compounds are listed in Table 3.

The octahedral position (12c) of Sn(IV) in the structure was confirmed by Mössbauer spectroscopy ($\text{DI} = -0.349\text{ mm s}^{-1}$) (Fig. 2).

3.1. EPR and TPR investigation

The lack of detailed structural information concerning the copper distribution in $\text{Cu}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ [2] led us to perform two complementary investigations:

(1) The EPR spectrum for $\text{Cu}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ (Q-band at RT) (Fig. 3) is not clearly defined but at least two signals were detected which can be related to two possible sites for Cu^{2+} ions in the structure. The EPR parameters ($g_{\parallel} = 2.28$ and 2.33 ; $g_{\perp} = 2.10$) are consistent with the localization of Cu^{2+} in either a square planar or a distorted polyhedral structure (local environment made up of five or six oxygen atoms).

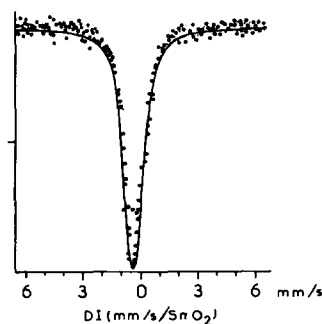
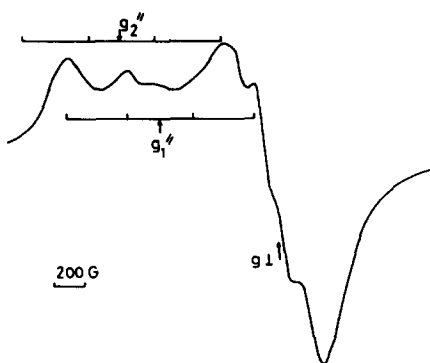
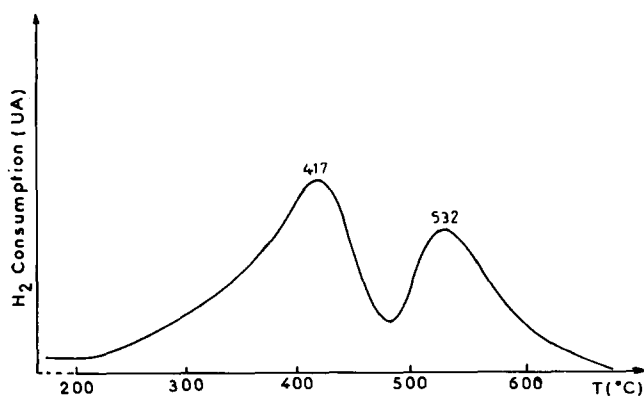
(2) Another procedure used to investigate this problem was temperature-programmed reduction (TPR) analysis of $\text{Cu}_{0.5}\text{Zr}_2(\text{PO}_4)_3$, prepared by method 2, at 700°C under a pressure, p_{H_2} below 10 mmHg. Under these experimental conditions, two peaks appeared under a pressure p_{H_2} below 10 mmHg at 417 and 532°C (Fig. 4). Hydrogen consumption corresponded exactly to complete reduction of Cu^{2+} to Cu^0 in two steps, without the occurrence of Cu^+ . This experiment confirms the Cu^{2+} distribution between two sites in an approximate ratio of 60 to 40%. The ease of reduction depends on the location of the Cu^{2+} ions in the structure. This result is in good agreement with the recent EXAFS study of this material [9].

3.2. Optical properties

(1) The diffuse reflectance spectra of $\text{Cu}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ samples are compared in Fig. 5(a). The single absorption band at about 250 nm ($\text{M} \equiv \text{Sn}, \text{Zr}$), slightly displaced in $\text{Cu}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ at 320 nm , can be assigned to

TABLE 3. Cell parameters for the compounds $\text{Cu}_{0.5}\text{M}_2(\text{PO}_4)_3$

M	Preparation method (1 or 2)	$a_m \pm 0.02$ (Å)	$b_m \pm 0.02$ (Å)	$c_m \pm 0.05$ (Å)	$\beta \pm 0.02$ (deg)
Ti [8]	(1)	14.57	8.41	17.52	123.60
Sn	(1 or 2)	14.62	8.44	17.82	123.10
Zr	(1)	15.31	8.84	18.28	123.9
Zr	(2) ^a	12.55 ± 0.01	8.898 ± 0.002	8.844 ± 0.002	$90.02 \pm 0.02^\circ$

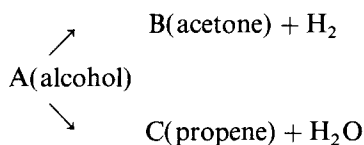
^a $\text{Sc}_2(\text{WO}_4)_3$ type.Fig. 2. Mössbauer spectra of $\text{Cu}_{0.5}\text{Sn}_2(\text{PO}_4)_3$.Fig. 3. EPR spectra recorded at 300 K (Q-band) for $\text{Cu}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ (method 2).Fig. 4. Temperature-programmed reduction of $\text{Cu}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ (method 2).

both the electron transfer reactions O^{2-} to M^{4+} and O^{2-} to Cu^{2+} . The large band located between 600 and 1400 nm corresponds to crystal field transitions of Cu^{2+} ions with apparent distortion of the copper sites.

(2) IR spectroscopy was used to characterize catalyst surfaces. For $\text{Cu}_{0.5}\text{Sn}_2(\text{PO}_4)_3$ and $\text{Cu}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ samples obtained by coprecipitation, the infrared spectra (Fig. 6) always showed one large band centred at 3400 cm^{-1} which could be assigned to OH stretching. These hydroxyl groups are of prime importance in the catalytic behaviour.

3.3. Catalytic activity

The catalytic activity of $\text{Cu}_{0.5}\text{M}_2(\text{PO}_4)_3$ ($M \equiv \text{Ti, Zr, Sn}$) was measured using isopropanol decomposition as a test reaction:



The runs were performed in a U-shaped continuous-flow microreactor. The experimental conditions were: $m_{\text{cat}} = 100\text{ mg}$; $p_{\text{alc}} = 15\text{ mmHg}$; $T_{\text{react}} = 190\text{--}240\text{ }^\circ\text{C}$.

The catalytic behaviour of the phosphates was found to depend on three factors: on the nature of the M(IV) element (Zr is the most complex) but especially on the method of preparation and the reaction temperature. Two cases may be compared:

(a) In general, phosphates $\text{Cu}_{0.5}\text{M}_2(\text{PO}_4)_3$ obtained by oxidation of Cu(I) compounds and added to isopropanol at $240\text{ }^\circ\text{C}$ showed little dehydrogenation or dehydration activity at steady state (respectively 0.5% and 3–6%) ($M \equiv \text{Zr} \rightarrow \text{Sn} \rightarrow \text{Ti}$) after 1 h of experiment. However, dehydrogenation activity increased slightly with the introduction of O_2 into the reactor (Figs. 7(a) and 7(b)). The selectivity was oriented towards the dehydration of the alcohol.

(b) With a catalyst prepared by the sol-gel method ($M \equiv \text{Sn, Zr}$), and so with a larger surface area, and particularly with $\text{Cu}_{0.5}\text{Zr}_2(\text{PO}_4)_3$, decomposition at the same reaction temperature ($240\text{ }^\circ\text{C}$) led to more complex results: strong adsorption of isopropanol occurred

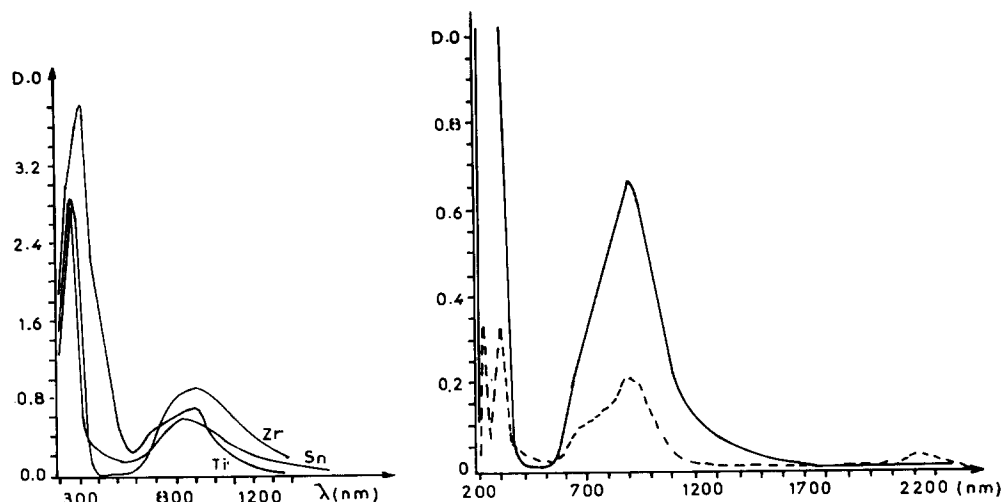


Fig. 5. Diffuse reflectance spectra of (a) $\text{Cu}_{0.5}\text{M}_2(\text{PO}_4)_3$ ($\text{M} \equiv \text{Zr, Sn, Ti}$); (b) $\text{Cu}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ (1): full line, before the catalytic run; dashed line, after the test.

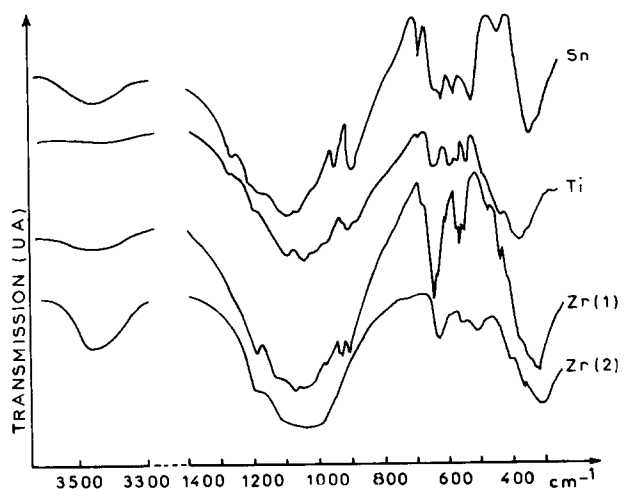


Fig. 6. Infrared absorption spectra of $\text{Cu}_{0.5}\text{M}_2(\text{PO}_4)_3$ ($\text{M} \equiv \text{Zr, Sn, Ti}$).

on the surface during the reaction; in addition a carbonaceous deposit appeared on the catalyst and there were also some products which were not identified by the chromatographic analysis.

Nevertheless, at lower temperatures (190°C) the reaction gave results similar to those obtained in the previous case (a) (Fig. 7(c)).

The characterization of the solids after the catalytic runs (essentially $\text{Cu}_{0.5}\text{Zr}_2(\text{PO}_4)_3$) was performed by X-ray diffraction, IR, UV-visible and X-ray photoelectron spectroscopies.

In the first case (a), the X-ray diffraction patterns indicated that the lattice symmetry became close to rhombohedral without any formation of metallic copper. The diffuse reflectance spectrum of $\text{Cu}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ showed a decrease in the intensity of the band centred

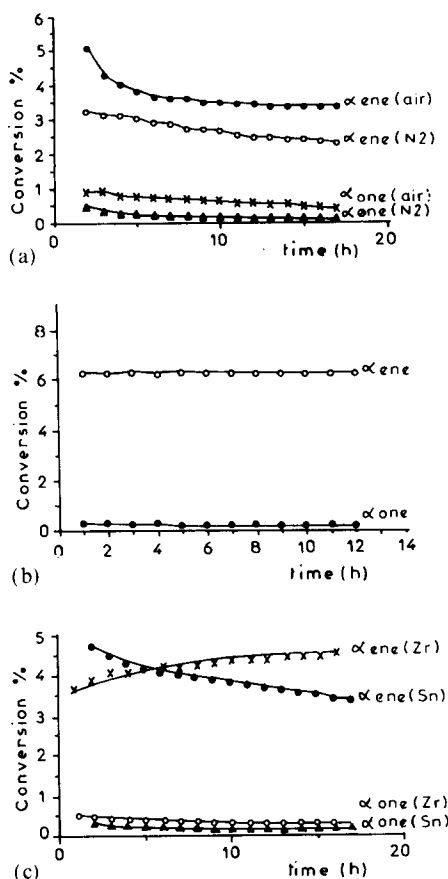


Fig. 7. Isopropyl alcohol conversion into acetone (α_{one}) and propene (α_{ene}) plotted vs. time, on (a) $\text{Cu}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ (1) at $T_{\text{R}} = 240^\circ\text{C}$; (b) $\text{Cu}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ (1) at $T_{\text{R}} = 240^\circ\text{C}$; (c) $\text{Cu}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ (2) and $\text{Cu}_{0.5}\text{Sn}_2(\text{PO}_4)_3$ (2) at $T_{\text{R}} = 190^\circ\text{C}$.

at 900 nm which, as mentioned above, was attributed to crystal field transitions of Cu^{2+} ions; and the emergence of a new peak at 300 nm was attributed to transition between the $(3d)^{10}$ and $(3d)^9(4s)^1$ Cu^+ levels (Fig.

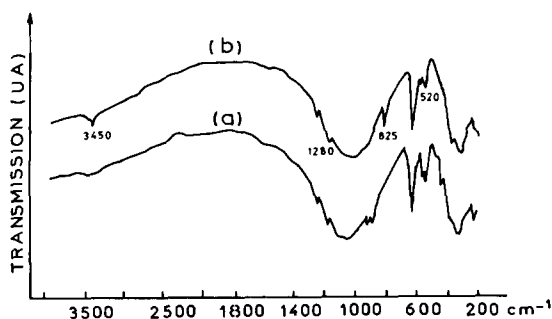


Fig. 8. Infrared absorption spectra of $\text{Cu}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ (1) (a) before catalytic test; (b) after catalytic test.

5(b)). Protonation of the sample during the reduction $\text{Cu}^{2+} \rightarrow \text{Cu}^+$ was demonstrated in the IR spectra by the appearance of OH bands showing the presence of $(\text{HPO}_4)^{2-}$ ions especially at 825 cm^{-1} ($\gamma\text{-P-OH}$) [10] (Fig. 8). These intercalated protons were more strongly bonded than those on the surface, as shown by the ^1H NMR study. The XPS spectrum also indicated that a significant proportion of the Cu^{2+} ions were conserved (Fig. 1(b)).

In the second case (b), at 240°C , almost all the Cu^{2+} ions disappeared according to the XPS and UV-visible spectra (Fig. 1(c)). It is reported, moreover, that on $\text{Cu}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ prepared at 500°C ($93 \text{ m}^2 \text{ g}^{-1}$), some Cu^0 species can appear as shown by the IR band at 2125 cm^{-1} obtained after CO adsorption on small Cu particles [11]. Finally, broadening of the OH band and the presence of H_2O were evident in the IR spectra of $\text{Cu}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ after the catalytic reaction.

4. Discussion

Characterization of the samples after the catalytic experiments showed that:

(1) In the case (a), the Cu^{2+} ions underwent a reduction to Cu^+ and the dehydrogenation activity dropped to a very low value. This activity was previously observed to decay in the first few minutes of the reaction [3], in the same way as the concentration of Cu^{2+} ions which are believed to be the active sites.

Addition of oxygen to the reactant mixture maintained the activity at its higher level because it prevented the lowering of the dehydrogenation activity and maintained the concentration of Cu^{2+} ions.

The dehydration activity is weak and seems to depend slightly on the nature of the element M.

(2) In case (b) with the samples which had the largest surface areas (Zr), the reduction during the reaction

seemed to be a more complex process since sometimes Cu^0 particles were detected in addition to Cu^+ ions. This is possibly related to the initial distribution of Cu^{2+} ions between the two sites in the structure, as observed previously. However, metallic copper does not influence the orientation of the selectivity. The behaviour of this type of sample as suggested by its predominant dehydration activity is governed by the acidity of its surface which can be attributed to P-OH groups formed at the surface or caused by hydrolysis of $(\text{HPO}_4)^{2-}$ ions during the reaction. These strongly acidic sites may be involved in the development of secondary reactions such as the deposition of polymers on the catalyst. This secondary behaviour, which was to be expected, taking into account the mode of preparation, is to be compared with that observed in gel forms of zirconium phosphates [12].

5. Conclusion

Copper(II) Nasicon-type phosphates with $\text{M(IV)} \equiv \text{Zr}, \text{Sn}, \text{Ti}$ were investigated and characterized by both solid state techniques and catalytic decomposition of alcohols. The acidic properties of the samples, especially those prepared by the sol-gel method, were so enhanced that the catalytic role of the copper was restricted and inhibited by the dehydration.

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