FULL PAPERS

Apatitic Tricalcium Phosphate as Novel Smart Solids for Supported Aqueous Phase Catalysis (SAPC)

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Abstract: Apatitic tricalcium phosphate was used as support for supported aqueous phase catalysis (SAPC) in the hydroformylation reaction of oct-1-ene, at 80 °C in toluene using a dinuclear rhodium complex bearing TPPTS as hydrophilic ligands. The reaction yield is maximum and constant when the hydration rate of the support is ranging from 20 to 35%, before starting to decrease dramatically. The support was examined initially and after catalytic runs by XRD, FTIR, ^{1}H and ^{31}P NMR, SEM and EDS. No change was observed when the hydration rate is less than 35%. Beyond 35%, some decomposition of the support into monetite and stoichiometric apatite occurred; the drop in the yield is essentially due to a loss of droplets of water from the support. The outstanding yield observed with the apatitic tricalcium phosphate, when compared to silica usually used in SAPC, was attributed to the orientation of the catalytic molecule arising from the adsorption of some of the TPPTS ligands onto the hydrophilic surface of apatite.

Keywords: apatite; hydroformylation; rhodium; supported aqueous phase catalysis; tricalcium phosphate

Introduction

Supported aqueous phase catalysis (SAPC) is an elegant method to perform catalysis under homogeneous conditions and simultaneously to separate the catalyst from the products.[1] Indeed, it consists of the adsorbance of a catalyst precursor dissolved in a thin film of water on the surface of a hydrophilic solid. The catalyst should present hydrophilic parts allowing its dissolution in the water film and thus its anchorage on the support. The rest of the catalyst is oriented towards the organic phase, the catalytic reaction taking place at the aqueous-organic interface. Supports with highly specific surface area allow an optimal spread out of catalyst to be obtained due to their high interfacial surface area. Various hydrated silicas with silanol Si-OH groups on the surface have been widely used until now.[2–7] Several catalytic reactions can be done using SAPC. Among them, the hydroformylation reaction of oct-1-ene to yield nonanal and 2-methyloctanal carried out in toluene using a specific dinuclear rhodium complex as a catalyst precursor and a silica support was studied.[8]

Other supports should be used if they present, as main characteristics, a strong hydrophilic character and a high specific surface area. For example, γ-alumina was used but the results were deceiving.[3] Curiously, no study has dealt with the use of calcium phosphates in this context, whereas some of them present simultaneously these two properties. Such is the case with deficient apatites, prepared by double decomposition, at room temperature.[9,10] Their general formula is: $Ca_{10-x}(PO_4)_{6-x}$ $(HPO_4)_x(OH)_{2-x}$ with $0 < x < 2$; among them apatitic tricalcium phosphate is the most stable. These apatites present a low level of solubility in water and are well known for their outstanding properties to adsorb mineral and organic anions or cations, and peptides or proteins as well.[11] Because of these properties, they are widely used in chromatographic column separations.

It seemed interesting to us to investigate whether apatitic tricalcium phosphate of the formula $Ca_9(PO_4)_5$ $(HPO_4)(OH)$ could be used as a support for SAPC. Indeed, prepared under the conditions described above, this material presents a specific surface area of around 85 m²/g and adsorbs easily water on its surface.[12,13] Thus, we performed hydroformylation reactions of heavy alkenes but using as the support tricalcium phosphate instead of silica. We examined the influence of added water, leading to an aqueous film at the surface, on the yield of the reaction. Then, we analyzed the solids after catalysis in order to check their stability during the reaction.

Results

Study of the Yield

Whatever the experiments and their duration, selectivity in aldehydes was 100%. The yield was determined for various hydration rates of apatitic tricalcium phosphate and is given in Table 1. The yield variation is given in Figure 1. It can be seen that a minimum of around 10% of hydration rate is necessary to observe any catalytic activity. A first maximum is observed at *ca.* 14% corresponding to a yield of 12%, followed with a decrease to 4% (15.5 w/w %). Then, a significant strong increase appears in the yield, since the variation between 15.5 and 20.2 for the hydration results in an increase from 4 to 50%. This level of activity (52% within the experimental error) is maintained until a hydration of 35% is reached, and can be compared to the activity of a silica, for instance DS22 silica, although it presents a larger specific surface area (317 m²/g),[15] for which the plateau is 32% under the same experimental conditions. Beyond this 35% value, the yield decreases regularly to reach 6% at 50% of water content; simultaneously, small droplets of water are observed in the medium, immediately after the stirring is stopped, so that a leaching of rhodium occurs from the support into this water phase for which the transfer phenomena are very poor.

It appears that the yield remains constant in a broad range for a calcium phosphate support, and provides an easy control of the stability when a small change in the hydration rate takes place, especially for a large scale production. Concerning the regioselectivity of the hydroformylation reaction, linearities near to 80% were observed along the experiments. The shape of the curve giving the yield as a function of the hydration rate, especially the presence of a first maximum of weak intensity, has been observed previously.[15]

Study of Samples Before and After Catalysis

Calcium and phosphate contents in the initial apatitic tricalcium phosphate sample were determined. They show that the atomic ratio Ca/P is equal to 1.5, the same as pure tricalcium phosphate. Samples after catalytic experiments were not chemically analyzed because calcium phosphates are practically insoluble either in the organic phase, or in water.

Figure 2 reports the X-ray diffraction patterns of two representative samples after catalytic tests, carried out with 20 (Fig. 2a) and 50 w/w % (Fig. 2b) hydration rates. Figure 2a shows the pattern of a poorly crystallized apatite when the hydration level of the support was less

Figure 1. Yield of the hydroformylation catalytic reaction as a function of the hydration rate for apatitic tricalcium phosphate.
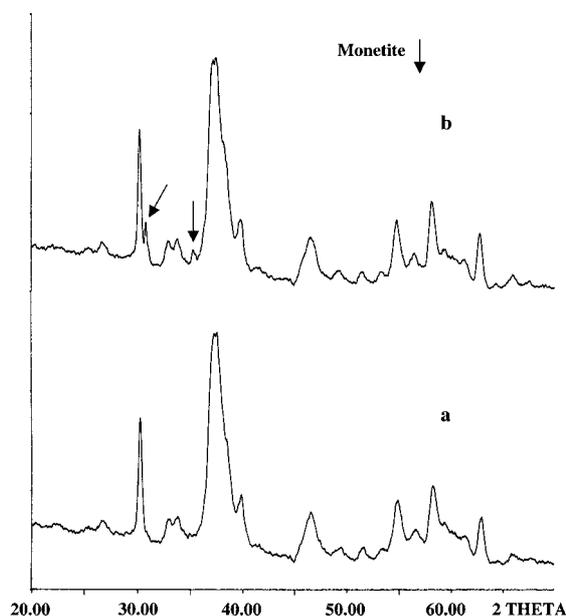
Figure 2. X-ray diffraction pattern of apatitic tricalcium phosphate samples after catalytic run carried out with a hydration rate of 20% (**a**), and 50% (**b**).

Table 1. Yields of the hydroformylation reaction of oct-1-ene as a function of the hydration rate.

Hydration rate	4.5	8.5	10.4	12.2	14.1	15.5	20.2	25.0	30.1	35.0	40.1	50.1
Yield [%][a]	0	0.4	2.0	8.4	12.0	4.0	50.0	52.0	54.2	50.3	36.8	6.3

[a] Errors in the yields: ± 2%.
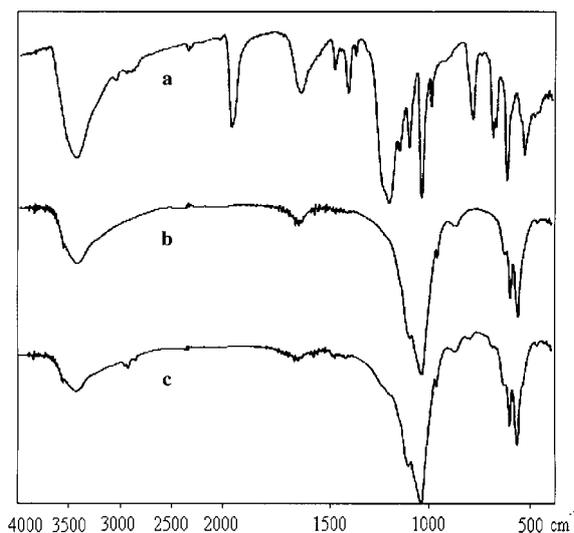
Figure 3. FTIR spectra in KBr pellets of the TPPTS rhodium complex (**a**), apatitic tricalcium phosphate sample itself (**b**), and after a catalytic run carried out with a hydration rate of 20% (**c**).

Figure 4. ^{1}H NMR spectra of apatitic tricalcium phosphate sample itself (**a**) and after a catalytic run with a hydration rate of 20% (**b**).

or equal to 35%. This pattern is quite the same as that of the initial sample. No structural changes occurred during the reaction. For higher hydration rates (see Fig. 2b), in addition to the apatitic phase, the peaks of monetite (CaHPO$_4$) appear.

FTIR spectra are shown in Figure 3. Spectra **b** and **c** correspond to the samples before and after catalysis carried out with 20 w/w % water, respectively. They present the bands of a calcium-deficient hydroxyapatite. The vibrations at 1100, 1036, 600 and 560 cm^{-1} are characteristic of PO$_4^{3-}$ groups in an apatitic environment. Other bands are detected at 875, 3560 and 630 cm^{-1}. The first one is due to HPO$_4^{2-}$ groups and the two others to OH$^-$ ions present in this calcium phosphate of general formula Ca$_9$(PO$_4$)$_5$(HPO$_4$)(OH). After catalysis (**c**), the most intense bands of TPPTS at ca 1220 cm^{-1} (spectrum **a** corresponds to the rhodium complex) gives rise to a shoulder of weak intensity consistent with its adsorption onto calcium phosphate.

NMR studies were carried out on initial sample of apatitic tricalcium phosphate and on the same sample after a catalytic run performed with an hydration rate of 20% (maximum yield).

Figure 4 shows the ^{1}H NMR spectra of the initial sample (**a**), and the sample after catalysis (**b**). For the initial sample, the broad line near 5.5 ppm corresponds to adsorbed water.[16–18] Its large width is due to its delocalization. It includes also the peak due to HPO$_4^{2-}$ ions of apatitic tricalcium phosphate.[17,18] The signal at − 0.1 ppm corresponds to OH$^-$ ions [16–18] sited in the tunnel of the apatitic structure and arising from the hydrolysis of PO$_4^{3-}$ ions into HPO$_4^{2-}$ and OH$^-$ ions. However, for the sample after catalysis, two additional sharp signals near 1.3 ppm appear whereas the peak due

to delocalized water, at 5.5 ppm decreases significantly in intensity. Such sharp peaks have been previously observed during the evolution of tricalcium phosphate gels,[18] and also with triclinic octacalcium phosphate.[17] The sharpness of these lines indicate that they correspond to a protonated species with a fixed location. They have been assigned to strongly fixed and localized water.[17] They cannot be due to the protons of the *tert*-butyl groups present in the [Rh$_2$(μ-S-*t*-Bu)$_2$(CO)$_2$ (TPPTS)$_2$] complex,[14] because of its very low amount as compared to those of apatitic calcium phosphate and water. Consequently, this study showed a strong interaction between the water film and the apatitic support in a large composition range where the yield is maximum.

Figure 5 reports the ^{31}P NMR spectra of the initial sample, and the sample after catalysis under the same conditions as above. An intense peak at 3 ppm can be assigned to PO$_4^{3-}$ groups, and the shoulder near 1 ppm to HPO$_4^{2-}$ ions in agreement with the observations by several authors on deficient apatites.[16–18] In this case too, the contribution of the rhodium complex or free TPPTS cannot be observed due to their very small amounts compared to those of apatite.

Three samples were examined by scanning electron microscopy (SEM): the initial sample, a sample after catalysis carried out at 20% hydration rate (maximum of yield), and another one after a catalytic run carried out at 50% (very low yield). The initial sample or the sample after catalysis at 20% present the same morphology: small grains of some tenths microns were observed (Fig. 6a). But, in the sample after catalysis at 50%, large plates of several microns can be seen, besides the grains (Fig. 6b). They are similar to those observed in the decomposition products of deficient calcium apatites in
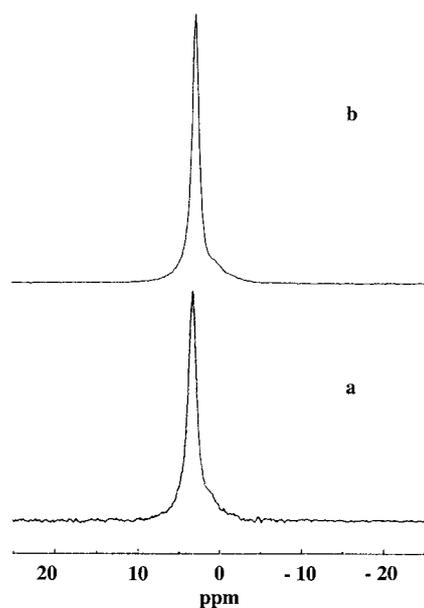
Figure 5. ^{31}P NMR spectra of apatitic tricalcium phosphate sample itself (**a**) and after catalytic run with a hydration rate of 20% (**b**).

a saturated wet atmosphere, and leading to monetite (large plates with an atomic Ca/P ratio of 1) and to stoichiometric apatite (Ca/P = 1.66). Microanalysis by energy dispersive spectroscopy (EDS) was performed on plates and grains: the spectra in energy show clearly that plates have a Ca/P ratio much lower than the grains (Figure 7). These observations are in agreement with the formation of monetite as observed by XRD. They are consistent with a decomposition of the apatitic tricalcium phosphate into monetite and hydroxyapatite, a phenomenon already observed for other deficient apatites in contact with a saturated wet atmosphere at 80 °C.[13] This reaction can be written as shown in Equation (1):

$$4\ Ca_9(PO_4)_5HPO_4(OH)\ +\ 2\ H_2O\ \longrightarrow$$

$$3\ Ca_{10}(PO_4)_6(OH)_2\ +\ 6\ CaHPO_4 \qquad (1)$$
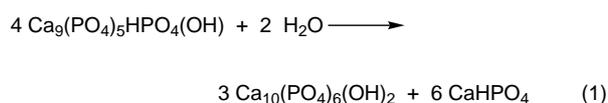
Interpretation and Discussion

This study shows that apatitic tricalcium phosphate is an efficient support in SAPC, and allows yields of *ca.* 50% to be obtained after 3 hours over a large range of hydration levels ranging between 20 and 35%. In this broad field of maximum yield, the water film remained firmly attached to the support. This is probably due to the strong interactions between water molecules and apatitic tricalcium phosphate, as evidenced by NMR.

Such an outstanding yield observed with the apatitic tricalcium phosphate support should be due to its
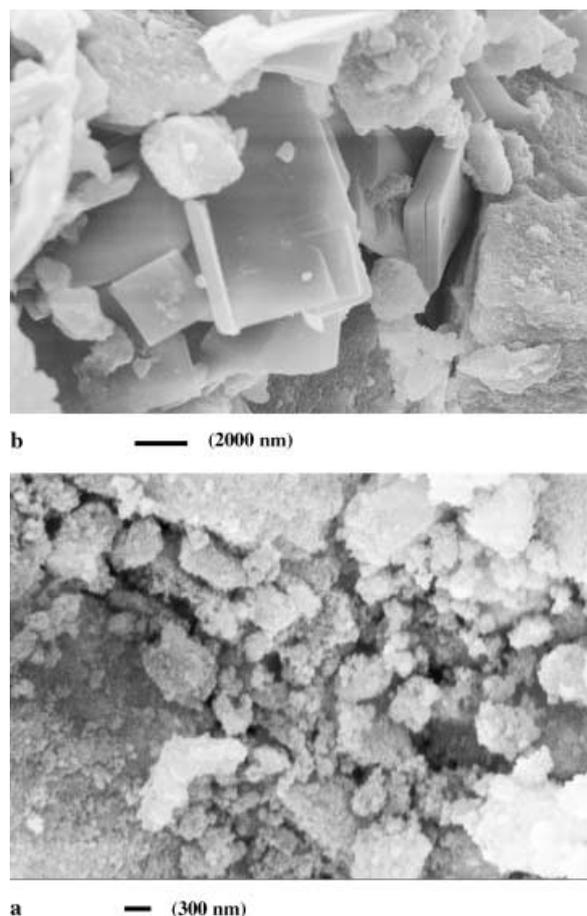
Figure 6. Scanning electron microscopy of apatitic tricalcium phosphate sample after catalytic run with a hydration rate of 20% (**a**) and 50% (**b**).

chemical reactivity. Indeed, apatites have excellent properties of adsorption towards mineral or organic cations or anions, (acetate, phosphate, sulfate, sulfonate, for example). We assume that, due to these adsorption properties, the rhodium complex (Figure 8) is oriented by the interaction of the three sulfonate groups of TPPTS with the calcium phosphate support: the hydrophobic part of the complex is turned towards the organic phase where catalytic reaction takes place. Such a representation is consistent with the apatitic structure. Indeed, the (110) plane (Figure 9) is characterized by a high density of calcium ions per surface area (4 ions for 65 $\AA^2$), with distances between the labelled ions of 6.44 or 6.88 Å and angles close to 60°. Interestingly, these values are near to those which were observed between the sulfonate groups in the molecule of TPPTS which presents a C_{3v} symmetry.

The question arises if a similar yield is obtained with other apatites. Experiments were carried out using, as support, a stoichiometric apatite prepared by double decomposition,[19] with the formula $Ca_{10}(PO_4)(OH)_2$, and the highest non-stoichiometric apatite, with the same Ca/P ratio of 1.33 as in triclinic octacalcium
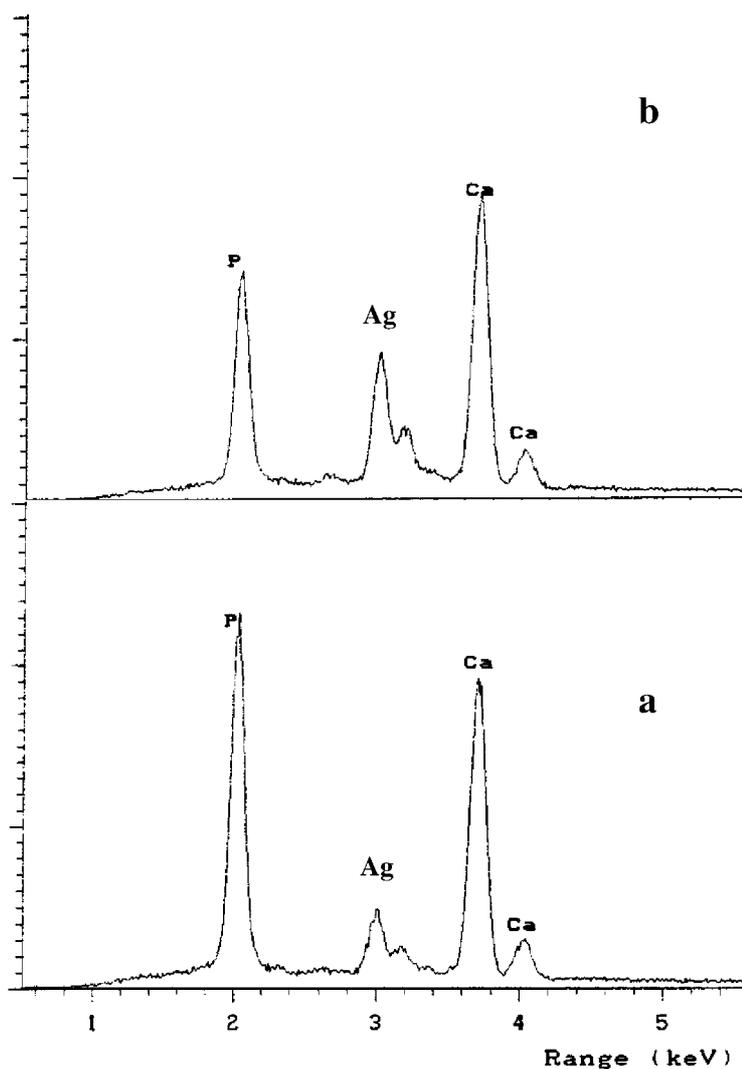
Figure 7. EDS microanalysis of apatitic tricalcium phosphate sample after catalytic run with a hydration rate of 50%: (**a**) plates; (**b**) grains.
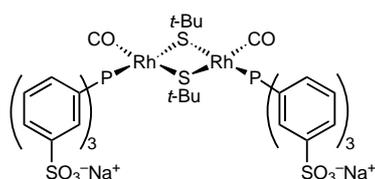
Figure 8. Schematic representation of the rhodium complex used in this study, with the two TPPTS ligands (triphenylphosphine trisulfonated-sodium salt.

Figure 9. Representation of the calcium ions in the (001) plane.

phosphate. This latter apatite, prepared in an water-ethanol medium, has the formula $Ca_8(PO_4)_{3.5}(HPO_4)_{2.5}(OH)_{0.5}$ and is called OCPap in the text. Preliminary experiments performed for 18 h run duration showed that the yield is very low, near to 1% with stoichiometric hydroxyapatite, but very high (93%) with the apatite having a Ca/P ratio of 1.33. These differences could be due in part to the HPO_4^{2-} content in this apatite, and consequently to the amount of water adsorbed (Table 2).

Experiments using other calcium phosphates with high content in HPO_4^{2-} such as monetite ($CaHPO_4$) or brushite ($CaHPO_4 \cdot 2\ H_2O$) as support showed very low yields. These compounds have a very low specific surface area (2 to 4 m^2/g) and lead to limited adsorptions.

This study has shown that the yield decreases when the hydration rate is higher than 35%. As mentioned

Table 2. Comparison of the reactivity of the three apatitic supports in SAPC for the hydroformylation of oct-1-ene.[a]

	HAP	PTCap	OCPap
HPO_4 content per cell unit	–	1	2.5
Initial water content	< 1 wt %	3 wt %	6 wt %
yield	0%	63%	93%

[a] Experimental conditions: 80 °C, 18 hours, hydration rate 16%, errors on the yields: ± 2%.

previously, this decrease is essentially due to a loss of water from the support leading to small droplets containing the catalyst. It can also be due in part to the limited decomposition of tricalcium phosphate into HAP and monetite, since both of these phosphates are not convenient for SAPC as has been shown before.

Conclusion

This study shows the unexpected use of calcium phosphates in the field of catalysis. Usually phosphates are introduced directly as catalytic solids, for instance, mixed phosphates of cerium and terbium.[20] They are also employed as supports for small metallic catalytic particles embedded at their surface. For the first time, we demonstrate that apatitic tricalcium phosphate is a very useful support for supported aqueous phase catalysis, and is much better than those used up to now. Furthermore, the richness of the chemistry of apatites could allow further developments since many possibilities for substitution are permitted by this structure. These results appear attractive and further work is in progress.

Experimental Section

Reagents

Reagents were calcium nitrate $Ca(NO_3)_2 \cdot 4\,H_2O$, and diammonium phosphate $(NH_4)_2HPO_4$ (Prolabo, analytical grade). Other reagents and solvents used in the synthesis of catalyst or in the catalytic tests were purchased from Aldrich and SDS, and used without further purification. Rhodium trichloride trihydrate and tris(*m*-sodium sulfonatophenyl)phosphine (TPPTS) were generous loans from Engelhardt-Comptoir, Lyon-Alemand-Louyot, and Hoechst (Ruhrchemie plant), respectively.

Apatitic tricalcium phosphate was prepared at room temperature, at pH 10, by double decomposition of calcium nitrate and diammonium phosphate.[9] After washing, the precipitate was dried at 80 °C overnight. Then, it was checked by the analytical techniques described below. Its composition corresponds to $Ca_9(PO_4)_5(HPO_4)(OH)$ and contains 3 w/w % residual water, as determined by the loss in weight after heating at 100 °C for 3 h.

The complex $[Rh_2(\mu\text{-S-}t\text{-Bu})_2(CO)_2(TPPTS)_2]$ was prepared as previously described.[14] by reaction for 15 minutes at room temperature of 2 equivalents of TPPTS with the complex $[Rh_2(\mu\text{-S-}t\text{-Bu})_2(CO)_4]$ dissolved in methanol.

Catalyzed Reactions

Catalytic tests were carried out in a 150 mL stainless steel stirred autoclave heated by a thermostatic oil bath. All tests were done with the same amounts of TPPTS (0.141 g, 2.27×10^{-4} mol), of complex $[Rh_2(\mu\text{-S-}t\text{-Bu})_2(CO)_2(TPPTS)_2]$ (0.038 g, 2.26×10^{-5} mol), 2.3 g of the support, 57 mL of toluene, and 2.86 g (2.55×10^{-2} mol) of oct-1-ene. Given amounts of deionized water, ranging between 0 and 1.5 mL, were added to reach the desired hydration level. It is worth mentioning that the values quoted correspond to the water content including the initial residual water on the support, and are expressed as w/w % with regard to the mass of the resulting hydrated support. In addition, all the experiments have been carried out with an initial organic phase (oct-1-ene + toluene) saturated with water (otherwise the experiments are not reproducible and are insignificant). The reactor was pressurized three times at 2 bar with an equivalent mixture of hydrogen and carbon monoxide. Then, the autoclave was pressurized at 2 bar with the same gas mixture, and the reactor was heated to 80 °C at 1870 rpm. The reactor was pressurized with 5 bar of syngas and the pressure kept constant for usually 3 hours at 5 bar inside the reactor. Then, the gas mixture feed was stopped and the reactor was cooled to room temperature. Finally, the reactor was depressurized and the liquid and solid phases were separated by filtration.

The organic phase was analyzed by gas phase chromatography on a Carlo Erba HRGC 5160 chromatograph equipped with a flame ionization detector and a capillary column Alltech Econopac FFAP (30 m; 0.53 mm; 1.2 μm), $T_{det} = 200$ °C, $P_{H_2} = 0.45$ bar.

Analytical Methods

Samples of apatitic tricalcium phosphate, before or after catalytic runs were analyzed by several techniques. The X-ray diffraction diagrams were obtained with a CPS 120 INEL diffractometer using the $K_{\alpha 1}$ line emitted by an anticathode of cobalt, ($\lambda = 1.78892$ Å). FTIR analyses covered the 4000 – 400 cm^{-1} region, on a Perkin-Elmer FTIR 1600 spectrometer with pellets of 1 mg of sample and 300 mg of KBr. NMR measurements were carried out on a Bruker MSL-300 NMR spectrometer operating at 120 MHz for ^{31}P and at 300 MHz for ^{1}H. About 150 mg of powder sample was packed into a zirconium rotor. All spectra were obtained by magic angle spinning (MAS). Chemical shifts were referenced to external 85% H_3PO_4. Morphology of samples was observed using a scanning electron microscope JEOL JSM-6400 after a slight metallization with silver. Local composition was estimated by energy dispersion analysis of the X-rays induced by the electronic beam (EDS). In addition, the initial sample was examined by chemical analysis after acidic dissolution (the level of calcium was determined by volumetric titration, and phosphorus by colorimetry of the phosphovanadomolybdenum complex), its specific surface area measured by BET

(Quantasorb) and its water content determined by loss in weight after heating at $100\,°C$ for 3 hours. Initial apatitic tricalcium phosphate sample shows a loss of 3% in weight, due to the removal of water adsorbed onto the surface.

Acknowledgements

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