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Specific tuning of acid/base sites in apatite materials to enhance their methanol thiolation catalytic performances

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ABSTRACT

Calcium hydroxyapatites (Hap) solids were prepared with various Ca/P atomic ratios, leading to stoichiometric $Ca_{10}(PO_4)_6(OH)_2$, calcium-deficient ($Ca/P < 1.67$) and calcium-rich materials. Their acid/base properties were tailored by the introduction of sodium and/or carbonate entities. The various hydroxyapatite solids were characterized by chemical analysis, IR, XRD and TGA techniques, and tested in methanol thiolation. The acid/base properties were evaluated using the isopropanol decomposition as a test reaction. Catalytic performances were found to be related to their acid/base properties. Total methanol conversion at 400 °C with high selectivity in methanethiol (60%) was obtained for the Na-CO_3 modified Hap.

1. Introduction

Thiochemistry is related to the synthesis of more than 30 compounds such as mercaptans, sulphides, sulphones, sulphoxides, thioacids and thioesters. Among them, mercaptans are one of the most important class of compounds because they are often used as starting materials for the synthesis of other thiocompounds [1]. Methanethiol, CH_3SH, also referred as methylmercaptan is produced in large amount because of its utilization in the first step of the commercial synthesis of methionine, an amino acid used as poultry feed supplement [1]. Industrially, methanethiol is currently prepared by direct thiolation of methanol over salts or oxides of alkali metals supported on alumina or acidic supports. Its synthesis from CH_3OH and H_2S needs a catalyst with high activity but also high selectivity since other products can also been formed, specially, CH_3SCH_3. According to Folkins and Miller [2], efficient catalysts for methanethiol conversion (80–90% selectivity at 350–420 °C) are alkali metal oxides or alkali metal carbonates deposited on alumina. Mashkina et al. [3] reported also that transition-metal oxides were more efficient when they are supported on alumina than on silica or silica-alumina. Indeed, the reaction between methanol and hydrogen sulphide involves acidic and basic sites. Mashkina et al. [4] have stated that the presence of basic sites can favor the formation of methanethiol, because methanethiol transforms to dimethylsulphide (CH_3SCH_3) if medium basic sites are close to strong Lewis acid sites (pairs of acid and base centers). Lavalley and coworkers [5] have studied various metals oxides (TiO_2, ZrO_2, Al_2O_3, MgO, . . .) as catalysts for methanol thiolation and found that the fewer the amount of basic sites, the higher was the selectivity to dimethylsulphide. Moreover, they showed that the highest basicity of MgO led to the lowest activity but also to a selective formation of methanethiol [5]. However, activity and selectivity did not appear to be simply related to basicity or acidity. Indeed, pairs of Lewis acid and base centers are involved in the reaction between methanol and H_2S [5]. More recently, El Ouassouli et al. [6] have reported that transition-metal sulphides supported on hydroxyapatite transform selectively dimethyldisulphide (CH_3SSCH_3) into CH_3SH, which was not the case when the metal sulphides were supported on alumina. This was explained by the presence of weaker acidic and basic Lewis sites on hydroxyapatite compared to alumina [6].

Calcium hydroxyapatites (Hap), with structural formula $Ca_{10}(PO_4)_6(OH)_2$ are handled as harmless solids to environment, they are thermally very stable and almost not soluble in water. When prepared under mild conditions, Hap can have interesting specific surface areas and porous volumes for catalysis purpose [7]. Moreover, their flexible structure allows the presence of defects, which can be obtained by ion substitution at either cationic or anionic sites [8].

In this work, we take advantage of this remarkable property to synthesize stoichiometric (Ca/P molar ratio = 1.67), calcium-deficient ($Ca/P < 1.67$) and calcium-rich ($Ca/P > 1.67$) apatites. The acid–base surface properties have been tailored introducing Na^+ or $CO_3{}^{2-}$ ions in the Hap structure during the preparation proce-

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dure. Characterizations (XRD, IR, TGA) have been performed and acid/base properties have been evaluated from the isopropanol decomposition reaction [9]. The catalysts, containing both acidic and basic centers of various strengths, have been tested in methanol thiolation.

2. Experimental

2.1. Catalysts preparation

All syntheses were carried out by the coprecipitation method. An aqueous solution of calcium nitrate (0.167 mol L^{-1}) was added dropwise for 3 h at around 100 °C to a solution of $(NH_4)_2HPO_4$ (0.1 mol L^{-1}) while stirring, the Ca/P molar ratio being equal to 1.67. The solution was adjusted to pH 10, by adding an ammonia solution. The resulting precipitate was slowly filtered, washed with hot water, dried under vacuum at 80 °C and calcined at 400 °C. Stoichiometric hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ (Hap) was then obtained. With the same procedure, calcium-deficient hydroxyapatite (HapD) with a general formula $Ca_{10-x}(HPO_4)_x(PO_4)_{6-x}(OH)_{2-x}$, where x represents cationic vacancies [10,11], was obtained adjusting the calcium nitrate concentration to obtain a solution with an Ca/P molar ratio equal to 0.9. As already reported, the Ca/P atomic ratio of the precipitate Hap did not match that of the solution of the initial reagents [12,13].

Sodium ions were introduced during the preparation procedure using a sodium nitrate precursor, dissolved in the calcium nitrate solution, the (Ca + Na)/P molar ratio was fixed to 1.67 for the synthesis of sodium-doped stoichiometric hydroxyapatite (Hap-Na) and to 0.9 for Ca-deficient hydroxyapatite (HapD-Na).

Stoichiometric carbonated hydroxyapatites (Hap-CO_3) and solids containing sodium ions (Hap-Na-CO_3) were obtained using the same coprecipitation procedure, but in which the Ca (+Na)/P molar ratio in the solution was fixed to 2. In this case, carbonate groups provided from atmospheric CO_2 could be introduced in the Hap structure [14].

Ca-rich hydroxyapatites (HapE) were also synthesized using a solution of $(NH_4)_2HPO_4$ (0.1 mol L^{-1}) added dropwise to a calcium solution (0.55 mol L^{-1}) while stirring, with an Ca/P molar ratio equal to 5.5. This high ratio allowed to introduce carbonate ions in the synthesized stoichiometric hydroxyapatite. The corresponding catalyst was denoted HapE-CO_3.

More carbonate ions were also introduced in an Ca-rich hydroxyapatite using sodium carbonate (5.83 g) dissolved in the ammonium hydrogenophosphate solution (0.1 mol L^{-1}). In this case, the resulting apatite was denoted HapE-Na-CO_3.

2.2. Characterization techniques

Chemical analysis was performed by the "Service Central d'Analyses du CNRS" (Vernaison, France).

TGA analyses were performed using a Thermal Analysis instrument (Model SDT 2960) on 20 mg of sample. Mass losses were recorded under synthetic air, with a heating rate of 4 °C min^{-1} from 20 °C to 800 °C.

The specific surface area of the catalysts was measured by N_2 physisorption using the BET method on a Quantasorb junior apparatus. A mass around 100 mg of sample was degassed at 150 °C for 45 min before measurements.

The crystal structure of solids was performed by X-ray diffraction (XRD) technique with a Siemens D5000 diffractometer equipped with a copper anode. The data were collected at 20 °C with a step size of 0.02° and a step time equal to 1.5 s. The patterns were collected over the 2θ range from 10° to 80°.

Transmission infrared (IR) spectra were recorded from 200 cm^{-1} to 4000 cm^{-1}, at room temperature, on a Nicolet 460 spectrophotometer. Samples were prepared by mixing 1 mg of powdered solid with 150 mg of dried KBr.

Catalytic tests were performed at 400 °C at atmospheric pressure (101.13 kPa) in an U-glass reactor filled with 200 mg of catalysts under a continuous flow of reactants: CH_3OH (4 cm^3 mn^{-1}) and H_2S (4 cm^3 mn^{-1}) diluted in CH_4 (4 cm^3 mn^{-1}). H_2S and CH_4 came from the decomposition at 400 °C of a flow of CH_3SSCH_3 on an NiMoP/Al_2O_3 catalyst (Axens, HR348), before mixing with the CH_3OH flow. CH_3SSCH_3 and methanol, were fed by bubbling hydrogen through saturators which temperature was fixed at 6 °C and 0 °C respectively. Reactant CH_3OH and products (CH_3SH and CH_3SCH_3) were analyzed using a gas chromatograph equipped with a flame ionization detector (FID).

f, the conversion, was calculated using the following equation:

$$f = \frac{a_{CH_3SH} + 2a_{CH_3SCH_3}}{a_{CH_3SH} + 2a_{CH_3SCH_3} + a_{CH_3OH}}$$

where a_y is the concentration of y.

Calculation formulae for methathiol selectivity s:

$$s = \frac{a_{CH_3SH}}{a_{CH_3SH} + 2a_{CH_3SCH_3}}$$

where a_{CH_3SH} and $a_{CH_3SCH_3}$ are the methanethiol and dimethylsulphide concentration respectively.

Acid/base performances of the various catalysts (100 mg) were evaluated using the isopropanol decomposition reaction at 275 °C. The catalytic reaction was carried out under inert atmosphere in a continuous-flow pyrex microreactor at atmospheric pressure. The feed was obtained by bubbling the argon (12 cm^3 mn^{-1}) through liquid isopropanol in a saturator at 0 °C. Products (propene, acetone and diisopropylether) were analyzed by gas chromatography equipped with an FID detector.

3. Results and discussion

Chemical composition values (Table 1) were found to be in agreement with the formation of an Ca-deficient apatite for HapD and HapD-Na solids, since the corresponding Ca/P ratios were found to be equal to 1.56 and 1.54 respectively, *i.e.* lower than the 1.67 value expected for a stoichiometric hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$. From chemical analysis, the number x of vacancies in the Ca-deficient HapD apatite, $Ca_{10-x}(HPO_4)_x(PO_4)_{6-x}(OH)_{2-x}$, [13,15], could be determined as 0.64 vacancy per 10 calcium ions. The Ca/P atomic ratios (rang-

Table 1
Chemical composition results and surface area of the hydroxyapatite materials.

Catalysts	Ca (wt.%)	P (wt.%)	Na (wt.%)	C (wt.%)	Ca/P (at./at.)	Specific surface area (m^2 g^{-1})
HapD	39.24	19.40	–	–	1.56	81
HapD-Na	38.85	19.49	0.44	–	1.54	78
Hap	37.10	17.45	–	–	1.64	79
Hap-Na	41.00	19.31	0.61	–	1.64	77
Hap-CO_3	39.10	18.45	–	0.33	1.63	107
Hap-Na-CO_3	38.10	18.30	0.52	0.33	1.60	106
HapE-CO_3	37.03	15.04	0	1.3	1.9	76
HapE-Na-CO_3	34.96	12.58	<0.02	2.9	2.1	77