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## ARTICLE TYPE

## The behaviour of an old catalyst revisited in a wet environment: Co ions in APO-5 split water under mild conditions

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## Abstract

Samples of the activated microporous aluminophosphate Co-APO-5, featuring *ca.* 20 % of Co<sup>3+</sup> cations, when immersed in water evolve molecular oxygen at room temperature in an endothermic process, without the need of either light or a sacrificial reactant. Successive drying of the sample at temperatures around 520 K releases molecular hydrogen, with recovery of the initial conditions. Several hydration/dehydration cycles may be performed without loss in activity, *i.e.* water is split in a thermal cycle under relatively mild conditions.

## Introduction

In recent years, an interest has grown for Co ions as active ingredients in the catalysts for the light-driven water splitting (WS), a reaction most promising for alternative energy sources.<sup>1</sup> Frei and co-workers<sup>2</sup> have shown that cobalt oxide Co<sub>3</sub>O<sub>4</sub> dispersed in SBA-15 silica catalyses, without any electrical bias, the photoreaction yielding oxygen from water, where the Ru<sup>++</sup>(bpy)<sub>3</sub> complex acts as a sensitizer, and the produced electrons are scavenged by Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>. Graetzel's group<sup>3</sup> in a different approach has proposed the use of hematite as a semiconductor where absorption of light can form electron/hole pairs then reacting with water: doping of hematite with Co ions has been, however, shown to be beneficial.

On the other hand, Nocera and co-workers have reported<sup>4</sup> that a system ITO/Co ions in a phosphate solution oxidizes water, with a remarkably reduced electrical bias. Recently, Nocera and associates have proposed a system where the electron/hole separation occurs in a Si wafer, employing nonetheless the same Co catalyst at the anode side.<sup>5</sup> Other very recent papers deal with the role in WS of Co(II) adsorbed on silica nanoparticles,<sup>6</sup> Co-oxide dispersed on graphene<sup>7</sup> and hematite nanorods,<sup>8</sup> as well as the effect of Co cations on the efficiency of WO<sub>3</sub> and BiVO<sub>4</sub> photoanodes.<sup>9,10</sup> Besides Co-containing solid phases, several Co-based molecular species were also found to act as homogeneous catalysts for water oxidation (WO).<sup>11-13</sup> The growing role of Co in the WS catalysts has been recently reviewed by Fontecave.<sup>14</sup>

From a general point of view, the reference chemistry is assumed to be that of the natural PSII system present in leaves or cyanobacteria, where a cluster of four Mn cations and one Ca cation acts as the catalytic centre.<sup>13-15</sup> high valence states are

reached by accumulating along a cycle four positive charges, then released in a single reactive event to oxidize water.<sup>14</sup> The catalyst by Nocera seems to have a "cubane" arrangement of Co(III) cations in a structure similar to that of PSII,<sup>16</sup> and is assumed to work in the same way. Similarly, according to Graetzel, oxidation of water implies at least two adjacent Co cation centres along a cycle<sup>3</sup> where unusually high valence states are reached. Also the reaction of Co<sup>3+</sup>-aquo complexes to yield oxygen seems to imply high valence states.<sup>17</sup>

On the spur of the growing interest for the role of Co cations in water splitting, we have undertaken a study of the reactivity towards liquid water of Co ions embedded in an insulator crystalline matrix, to define the chemistry of such ions in controlled coordinative and valence state. The first choice has been the porous aluminium phosphates (APO systems): other systems will follow. A popular APO system is that showing the AFI structure (APO-5), a structure with no zeolite analogue, composed by 4-, 6- and 12-ring straight channels interconnected through 6-ring windows. The main channels are almost circular with a free diameter of 7.3 Å (Scheme 1).

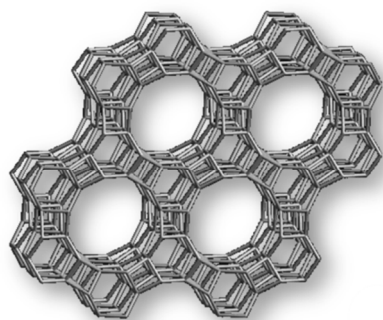
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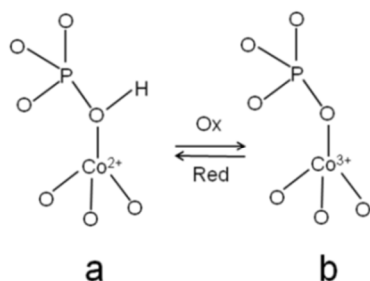
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Scheme 1. AFI structure of APO-5 view along the 001 direction [adapted from <http://www.iza-structure.org/>].

In APO systems, various divalent or trivalent cations can substitute for Al (originating the so called Me-APO systems), in particular both  $\text{Co}^{2+}$  and  $\text{Co}^{3+}$ . When trivalent cation substitute for Al, electroneutrality is preserved. In the case of divalent cations, like  $\text{Co}^{2+}$  for instance, a charge-balancing chemical object (*e.g.* a proton) is present:<sup>18</sup> this brings about the presence of an acidic hydroxyl (bridged  $\text{Co}^{2+}\text{--O(H)P}$  groups, Scheme 2a). Redox treatments can convert at least a fraction of the cations in Me-APO-5 from oxidation number II to III and vice versa (Scheme 2).



Scheme 2. Reversible redox process concerning tetrahedral Co ions within Co-APO-5 framework [adapted from ref. 18].

This is the effect, in particular, of the treatment under flowing oxygen to eliminate the structure directing agent (SDA), which converts to  $\text{Co}^{3+}$  15-20% of the  $\text{Co}^{2+}$  originally present.<sup>19</sup>

The nature of Co species in Co-APO-5 has been long debated, and studied through a variety of experimental techniques: the precise state of Co ions in the APO matrix is not, however, the subject of the present work. Note that in the present paper, both low Co contents and mild procedures of activation were chosen, so to avoid the intricacies that may arise under different circumstances. The mild activation temperatures adopted in this work should avoid, for instance, formation of i) defects, *i.e.* oxygen vacancies in the proximity of cobalt sites, as previously observed in Co-APO-5 outgassed at high temperature (873 K) or treated in hydrogen atmosphere at 673 K;<sup>20</sup> ii) sites able to abstract electrons from adsorbed species, as observed in zeolites/organic molecules systems, in which photo- or thermally induced electron transfer from adsorbed organic molecules (with

low ionization potential) to the zeolite has been documented in the literature.<sup>21,22</sup> Also, Co-APO-5 systems have been used as catalysts in many reactions, involving sometimes simultaneously both redox and Brønsted functionalities:<sup>23-26</sup> dry conditions were always adopted or, at the most, interaction was studied with water vapour.<sup>19,20,27,28</sup> Their chemistry towards water and, in particular, their behaviour in the water splitting reaction have never been examined.

The present work deals with the reactions of calcined Co-APO-5 with liquid water at room temperature without any illumination, electrical bias or sacrificial reactants. An endothermic formation of gaseous oxygen and a simultaneous drop in the pH of the suspension were observed. To understand such phenomena, the Co-APO-5 sample both before and after reaction was studied by means of DR-UV-Vis (Diffuse Reflectance Ultra Violet), FT-IR (Fourier Transform Infra Red) and X-ray Photoelectron (XPS) spectroscopies, as well as adsorption microcalorimetry. Drying of the sample was studied in a TPD (Temperature Programmed Desorption) experiment, by using an instrument coupled to a Mass Spectrometer.

## Experimental Section

The Co-APO-5 material was synthesized according to the sol-gel procedure reported in ref. 29. In a typical synthesis, N,N-diethylethanolamine (DEA) was used as template, standard Al and P sources were used, and Cobalt acetate was added to the gel phase, so that its nominal composition was 0.9  $\text{Al}_2\text{O}_3$  : 1.0  $\text{P}_2\text{O}_5$  : 0.1  $\text{CoO}$  : 1.6 DEA : 80  $\text{H}_2\text{O}$ . The gel was left to crystallize inside a Teflon-lined autoclave at 473 K for 3 days; the organic template was then removed by calcination under flowing oxygen at 823 K. Cobalt content in the fresh catalyst was *ca.* 3.0 wt. %, as determined by ICP-AES technique (Perkin Elmer OPTIMA 7000 DV ICP/OES).

The good quality of the prepared Co-APO-5 material was checked by means of  $\text{N}_2$  adsorption/desorption at 77 K, X-Rays powders Diffraction, FE-SEM (Field Emission Scanning Electron Microscopy), UV-Vis Spectroscopy, the related results being published elsewhere.<sup>30,31</sup> In summary, XRD and BET data, as well as FE-SEM micrographs showed that the as-synthesized sample was highly crystalline, with crystals of micrometric dimensions and no evidence of other phases besides Co-APO-5. Such crystalline structure is stable to reaction with water. Its blue colour is characteristic of tetrahedral  $\text{Co}^{2+}$  ions. The UV-Vis spectrum of the material shows a typical triplet of bands of tetrahedral  $\text{Co}^{2+}$  ions due to the  $4\text{A}_2 \rightarrow 4\text{T}_1(\text{P})$  transition is seen (18518, 17240 and 16000  $\text{cm}^{-1}$ )<sup>30,31</sup> when the template is present. The as synthesised sample was calcined for 10 h at 823 K in oxygen flow, to remove the template: the resulting powder was used for both further experiments and physico-chemical characterization. Calcination induces a colour change to grey-green, because of oxidation of some  $\text{Co}^{2+}$  ions to the tetrahedral  $\text{Co}^{3+}$  state, as monitored in the UV-Vis spectra (curve a in Figure 1) by a decrease in the overall intensity of the triplet in the visible region, and the growth of intense bands in the UV region above 20000  $\text{cm}^{-1}$ .

To measure evolved oxygen, 2.0 mL water were previously purged by flowing pure Ar for 30 min and then were contacted with the powder sample. The amount of evolved O<sub>2</sub> was into a Digital Model 10 Clark's cell (Ranks Brothers LTD): the Clark's cell temperature was maintained constant during the measurement by circulating water around the reactor.

Powders X-ray diffraction (XRD) patterns were collected on a X'Pert diffractometer (Phillips) using Cu K $\alpha$  radiation (1.541874 Å), scan range 5° - 45° 2 $\theta$ , step width 0.01°. Diffuse reflectance (DR) UV-Vis spectra were recorded on *ca.* 200-300 mg powder samples (CARY-500 UV-Vis-NIR spectrophotometer equipped with an integrating sphere, Varian Instrument).

XPS measurements were carried out on a PHI Model 5000 electron spectrometer equipped with an aluminium anode (1486 eV) monochromatic source. Samples were in the form of pellets previously outgassed at 573 K. To reduce possible charging effects of X-rays, a dual beam charge neutralization method was applied, combining both low energy ions and electrons. The Al 2p line at 74.5 eV was used as internal reference for BE determination. XPS intensity ratios were determined from the total integrated areas of Co 2p<sub>3/2</sub> and Al 2p lines.

For IR measurements, powder samples were pressed into thin, self-supporting wafers and pre-treated under high vacuum (residual pressure < 10<sup>-3</sup> mbar) using a standard vacuum frame, in a quartz cell equipped with KBr windows. IR spectra were collected at 2 cm<sup>-1</sup> resolution on a Bruker Equinox 55 FT-IR spectrophotometer, equipped with a MCT (Mercury Cadmium Telluride) detector. CO adsorption at nominal 77 K was studied on the calcined sample outgassed at 423 K and, after reaction with water, on the sample dehydrated at 323 K. Microcalorimetric measurements were carried out by means of a Setaram Calvet-type instrument, operated at 303 K. The microcalorimeter was equipped with a volumetric attachment of conventional design for gas dosage and measurement of the corresponding adsorbed amounts: two different doses of water vapour were contacted to the calcined sample (water partial pressures corresponding to 0.5 and 5 mbar, respectively).

## Results and Discussion

### Reaction of Co-APO-5 with liquid water

In a typical experiment, the calcined powder (0.5 g Co-APO-5 with 3% wt. Co, as determined by ICP-AES analysis<sup>30</sup>) was first outgassed at 423 K, then contacted with 2.0 mL bi-distilled, oxygen-free water inside a glass reactor, from which air had been previously removed by flowing Ar for 30 min. The formation of bubbles was observed after a few seconds, and O<sub>2</sub> evolution lasted for about 30 s: moles evolved at this stage were *ca.* 12\*10<sup>-6</sup>. The same experiment was run with 0.5 g APO-5, but no gas evolution was observed.

The pH of the system, initially at 5.6, dropped to 3.9 at the end of the experiment. Addition of NaOH solution to the suspension, bringing the pH value to 8.0, was observed to restart the reaction.

Upon reaction with water, the greenish powder turned blue, the typical colour of Co<sup>2+</sup> species. After completion of the reaction, the sample was dried and re-outgassed at 423 K: the corresponding DR-UV-Vis spectrum is reported in Figure 1 (curve c) along with that of the calcined sample (curve a) and that of the water treated sample, after mild dehydration at room temperature (curve b).

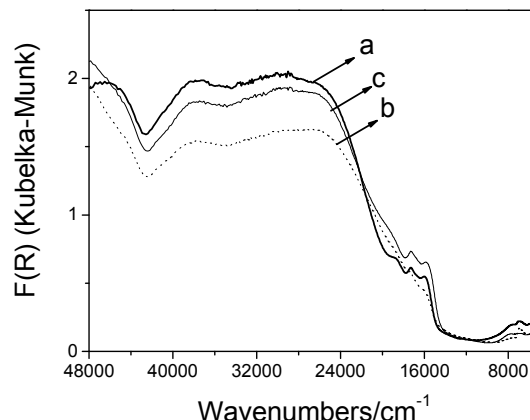
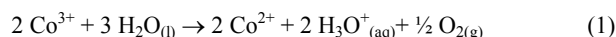


Figure 1. DR-UV-Vis spectra of Co-APO-5 powder: (a) calcined sample; (b) sample recovered after reaction with liquid water and mild dehydration by evacuation at room temperature; (c) sample dehydrated at 423 K (c).

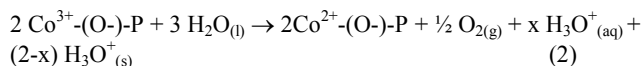
Calcined Co-APO-5 shows a triplet of bands between 20000 and 14000 cm<sup>-1</sup> assigned to the d-d transitions of Co<sup>2+</sup> ions in tetrahedral environment,<sup>20,32</sup> whereas the strong bands in the UV region are assigned to ligand-to-ion charge transfer (CT) bands of Co<sup>3+</sup> ions (curve a, Figure 1). In the water-reacted sample, after mild dehydration by evacuation at room temperature (curve b), the bands due to Co<sup>3+</sup> species are seen to decrease, and almost completely restored after mild outgassing at 423 K (curve c). Changes in intensity of the Co<sup>2+</sup> triplet bands are difficult to appreciate, because of the likely presence of water molecules changing the coordination of Co<sup>2+</sup> species. The overall evidence is that reduction is observed of Co<sup>3+</sup> to Co<sup>2+</sup> species by effect of water. This, together with the decrease in pH and the evolution of gaseous oxygen strongly suggests that reaction (1) is taking place:



The amount of evolved Oxygen corresponds to a fraction of Co<sup>3+</sup> sites about 19% of the total Co sites: this is what expected on the basis of the overall cobalt content in the studied sample.<sup>33</sup> If all protons given rise were present as hydronium ions, the pH expected value would be 1.6. Instead, the reaction stops at pH 3.9. It should be noted that the measured pH value concerns the bulk of the solution, whereas hydronium cations are most likely to be located close to the negative oxygen anions of the lattice, which would explain the discrepancy between the two values. Moreover, it should be considered that when dealing with a powder material dispersed in aqueous solution, its surface charge, and related protonation-deprotonation equilibria, strongly depends on pH. For instance, very acidic zeolites, like H-ZSM-5,



have points of zero charge in the 3-4 pH range,<sup>34,35</sup> leading to the conclusion that only a (limited) fraction of acidic sites in Co-APO-5 may be deprotonated in the adopted experimental conditions. Therefore, taking into account the presence of phosphate ligands around the Co centre and the partial deprotonation at pH = 3.9, reaction (1) can be re-written as:



in which the fact that only a fraction of the formed hydronium ions is in solution and the rest is at the solid surface is taken into account.

The dry chemistry of APO systems shows that the species  $\text{Co}^{2+}(\text{O-})\text{-P}$  can be considered as the conjugate base of the acid  $\text{Co}^{2+}(\text{OH})\text{-P}$ , the species shown in Scheme 2. The acidic nature of such species is well documented by IR experiments, as well as by its role in catalytic processes. Below, it is shown that it also plays a paramount role in the WS process under study. Catalytic results suggests that it is a strong acid, as far as gas-phase processes are concerned. We propose here that such species is also a strong acid in the Brønsted-Lowry sense towards water:

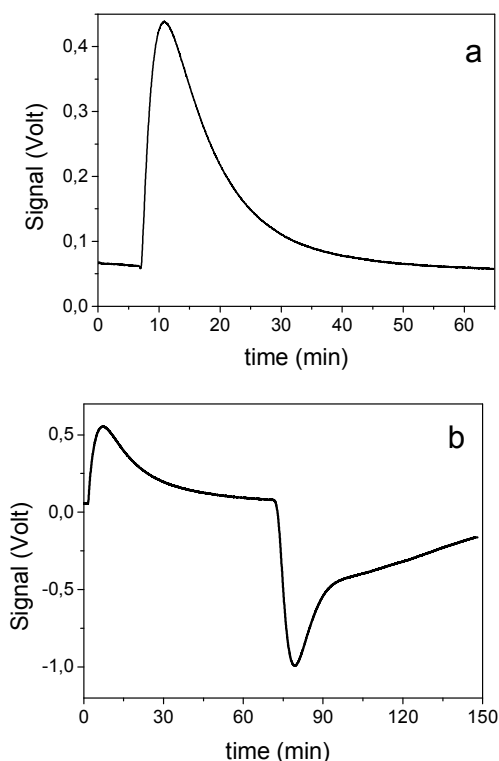
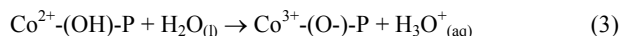


Figure 2. Heat evolution peaks as a function of time obtained after: (a) first dose of water vapour on calcined Co-APO-5, yielding a positive (exothermic) peak; (b) a dose of water vapour at later stages: a positive (exothermic) peak is seen initially (adsorption), followed by a negative (endothermic) one (reaction).

Because of the reaction, the glass bulb containing the suspension becomes cold, so indicating that the overall process is endothermic. This feature has been investigated by means of microcalorimetry, by dosing increasing amounts of water from the gas phase.

Figure 2 shows two examples of heat evolution curves, recorded at low (a) and high (b) water coverage. It is observed that, in the former case, heat evolution is exothermic (positive peak in Fig. 2a), as expected for any adsorption phenomena. Only at relatively high water coverage (Fig. 2b), after an initial exothermic step, an endothermic process sets in (negative peak in Fig. 2b). We take this as evidence that reaction (1) does not take place with water molecules plainly coordinated to the Co centre, but that water in the liquid form is required, probably to solvate the proton formed. This is shown by both the fact that at a low water coverage the same phenomenon was not observed and by the delay in the appearance of such endothermic peak as compared to reaction with liquid water, due to diffusion of water vapour within Co-APO-5 pores. Differences in the energetic of interaction of zeolite and zeolite-like materials with either gaseous or liquid water are not surprising: theoretical calculations have shown, for instance, that the reaction of hydrogarnet defects in chabasite and sodalite is exothermic when water is in the gas phase and endothermic when it is in the liquid phase.<sup>36</sup>

From a strictly thermodynamic point of view, the endothermic nature of the reaction does not prevent it from being spontaneous, because gaseous oxygen is produced and also hydronium ions enter the solution. Both features are likely to increase substantially the standard entropy change of reaction. Although the picture concerning liquid water reaction with Co-APO-5 seemed clear enough, further steps were taken to investigate the oxidation state of surface Co.

#### XPS and IR study of the sample before reaction with liquid water and after mild ambient dehydration.

According to the literature, the oxidation states of cobalt in oxides and massive materials may be discriminated on the basis of their XPS spectra.<sup>37,38</sup> Instead, as it concerns Co-containing zeolites and APOs, very few reports are available:<sup>39,40</sup> for this reason, the interpretation proposed is tentative, although validated by IR and UV-Vis results.

Figure 3 reports XPS spectra both before and after the reaction with liquid water: Co 2p XP spectra (Figs. 3a and 3b) are rather noisy and careful curve-fitting is required to extract information. Before reaction (Figure 3a), the signal due to  $\text{Co}^{2+}$  ( $2p_{3/2}$ ) is at 780.88 eV, together with a satellite at 785.99 eV; that of  $\text{Co}^{2+}$  ( $2p_{1/2}$ ) is at 796.93 eV with a satellite at 801.57 eV. Both satellite bands are very intense, as usual for  $\text{Co}^{2+}$  paramagnetic ions.<sup>41</sup> The distance between Co ( $2p_{3/2}$ ) and Co ( $2p_{1/2}$ ) lines is 16.05 eV. Usually, a value larger or equal to 15.5 eV indicates the presence of well dispersed  $\text{Co}^{2+}$  species, whereas when mixed  $\text{Co}^{2+}/\text{Co}^{3+}$  phases are present, the difference in energy decreases to 15 eV. We take the value measured in the present case as a suggestion of well dispersed Co sites within the APO-5 matrix.

For a satisfactory fitting a band at 782.66 eV is needed (shaded band in the Figure), which we ascribe to  $\text{Co}^{3+}$  ions, for which component no satellite band is expected, because of the diamagnetic nature of  $\text{Co}^{3+}$  ions. After reaction (Figure 3b), the location of the signals does not appreciably change: the lines due to  $\text{Co}^{2+}$  ions become more intense and, correspondingly, the area of  $\text{Co}^{3+}$  peak is seen to. Taking into account the heavy uncertainties related to spectral resolution, this finding can be considered in agreement with the above picture.

The O 1s spectrum of the calcined sample (dotted curve in Figure 3c) only shows a symmetric peak centred at 531 eV, a value considered typical for O in the APO framework;<sup>39</sup> the presence of other phases may thus be ruled out. Should other kinds of O atoms be present, the peak would have a second component at *ca.* 529 eV.<sup>39</sup> Indeed, after reaction with water a shift to 532 eV is observed, assigned to oxygen atoms in hydroxide species,<sup>42</sup> without any appreciable change in peak intensity and a band at *ca.* 536 eV shows up, due to water.<sup>42</sup>

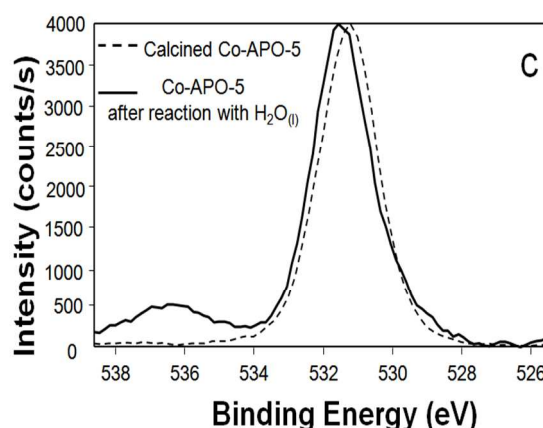
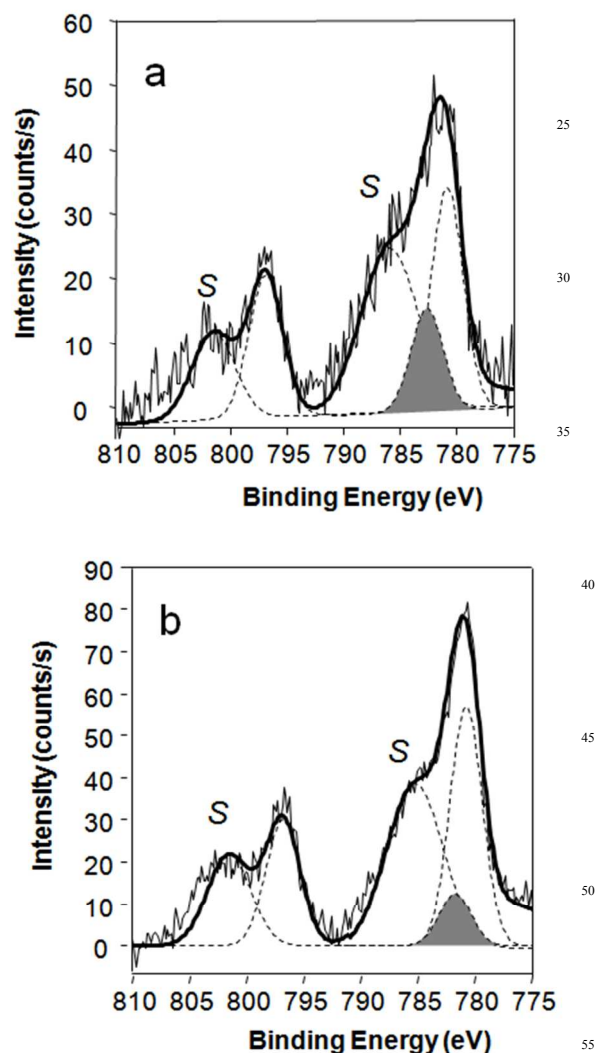


Figure 3. Co 2p XP Spectra of calcined Co-APO-5 (a) and Co-APO-5 after reaction in water (b); the letter S indicates satellite bands. O 1s XP spectra of calcined Co-APO 5 (dotted curve) and Co-APO-5 after reaction in liquid water (c).

In summary, XPS data confirm the conclusions drawn from other techniques: i) in Co-APO-5, Co ions are well dispersed and no aggregated phase is likely to occur; ii) in the calcined sample, Cobalt occurs primarily as  $\text{Co}^{2+}$  ions, while a substantial fraction is  $\text{Co}^{3+}$ ; iii) after water oxidation, part of  $\text{Co}^{3+}$  ions is reduced back to  $\text{Co}^{2+}$ ; iv) in the O 1s region, besides the presence of water after reaction in liquid phase, a shift of the main band to higher BE is observed, due to the formation of hydroxyls species.

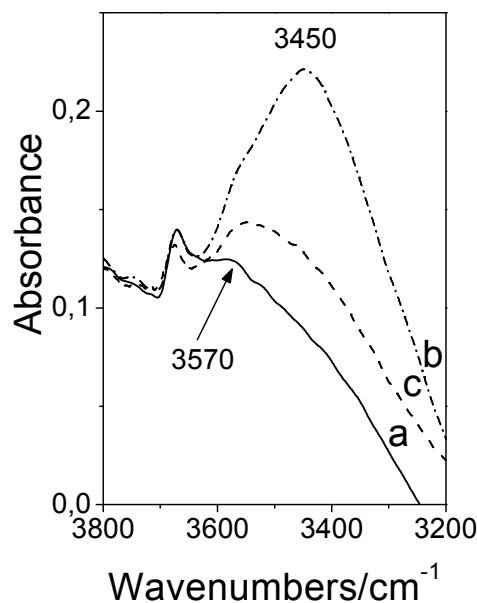


Figure 4. IR Spectra in the O-H stretching range (3800-3200  $\text{cm}^{-1}$ ) of Co-APO-5 self-supporting wafer: (a) calcined sample; (b) sample after reaction in water; (c) sample reduced in  $\text{H}_2$  at 623 K.

IR spectra of the sample before and after reaction with water were studied in two regions: (i) that of O-H stretch, between 3800

and  $3200\text{ cm}^{-1}$ ; and (ii) the stretching region of CO, in the  $2250 - 2050\text{ cm}^{-1}$  range. Figure 4 compares the IR spectra in the OH-stretching region of three types of sample: that calcined, before (curve a) and after reaction with water (curve b), and the same sample reduced in gaseous  $\text{H}_2$  at  $673\text{ K}$  according to a standard procedure (curve c). Because the presence of liquid water prevents obtaining IR spectra, the reaction with water of Co-APO-5 was carried out by saturating the calcined sample with water vapour and excess water was removed by outgassing at about  $323\text{ K}$ .

Spectrum (a) shows a main band at  $3671\text{ cm}^{-1}$ , with a less defined peak at *ca.*  $3570\text{ cm}^{-1}$ . The former is assigned to defect-related P-OH groups, the latter to hydroxyl species bridged over Co and P atoms of the type  $\text{Co}^{2+}\text{-(OH)-P}$  as in Scheme 2.<sup>18</sup> The IR spectrum of the sample reduced in  $\text{H}_2$  (curve c) shows that, as expected, the band due to bridged groups is more intense than with the calcined sample. After water contact (curve b), the P-OH band is unchanged, whereas the absorption due to  $\text{Co}^{2+}\text{-(OH)-P}$  groups is greatly enhanced. The band at  $3570\text{ cm}^{-1}$ , due to the naked  $\text{Co}^{2+}\text{-(OH)-P}$  species is now a shoulder of a prominent component at about  $3450\text{ cm}^{-1}$ , due to the same  $\text{Co}^{2+}\text{-(OH)-P}$  species, the hydroxyl moiety of which is involved in H-bonding with residual water.

The presence of adsorbed water did not allow a clear estimate of the increase in the population of acidic  $\text{Co}^{2+}\text{-(OH)-P}$  species, which can be instead appreciated in the following experiment: Figure 5 describes the changes brought about by the reaction with water, as monitored by the IR spectra of CO adsorbed at nominal  $77\text{ K}$ . After CO adsorption on the calcined sample (Figure 5a), a sharp band is seen at  $2186\text{ cm}^{-1}$ , due to CO molecules interacting with extra-framework  $\text{Co}^{2+}$  ions.<sup>43</sup> A less intense absorption occurs at  $2164\text{ cm}^{-1}$ , due to CO molecules interacting with bridged hydroxyls. Note that the frequency value is indicative of the acidic nature of the  $\text{Co}^{2+}\text{-(OH)-P}$  species.

At higher CO partial pressures, IR spectra are dominated by the band due to physisorbed CO at  $2139\text{ cm}^{-1}$ , not really relevant here.

Dosing CO at a nominal temperature of  $77\text{ K}$  on water-treated and subsequently dried Co-APO-5 (Figure 5b) brings about the formation of bands at  $2220$ ,  $2186$ ,  $2170$  and  $2139$  (liquid-like)  $\text{cm}^{-1}$ . The band at  $2220\text{ cm}^{-1}$  is due to CO molecules interacting with some EFAL (extra-framework Al) sites.<sup>44</sup> their formation is likely due to the fact that the sample was merged in water. The IR band at  $2220\text{ cm}^{-1}$  is expected to be relatively intense, so that it can be inferred that the population of EFAL in this sample is low and its role in the overall chemistry negligible. Moreover, such a high CO frequency indicates that the Al cations kept the  $+3$  oxidation number, thus probably not influencing the oxidation number of Co species. The band at  $2186\text{ cm}^{-1}$  is due to CO adsorbed on  $\text{Co}^{2+}$  cations, already observed in the calcined sample (Figure 5a). The massive presence of  $\text{Co}^{2+}\text{-(OH)-P}$  species is shown in this case by the relative intensity of the band due to interaction of CO with the bridged species (band at  $2169\text{ cm}^{-1}$ ), which is more intense as compared to that at  $2186\text{ cm}^{-1}$ .

2166  $\text{cm}^{-1}$ ), which is more intense as compared to that at  $2186\text{ cm}^{-1}$ .

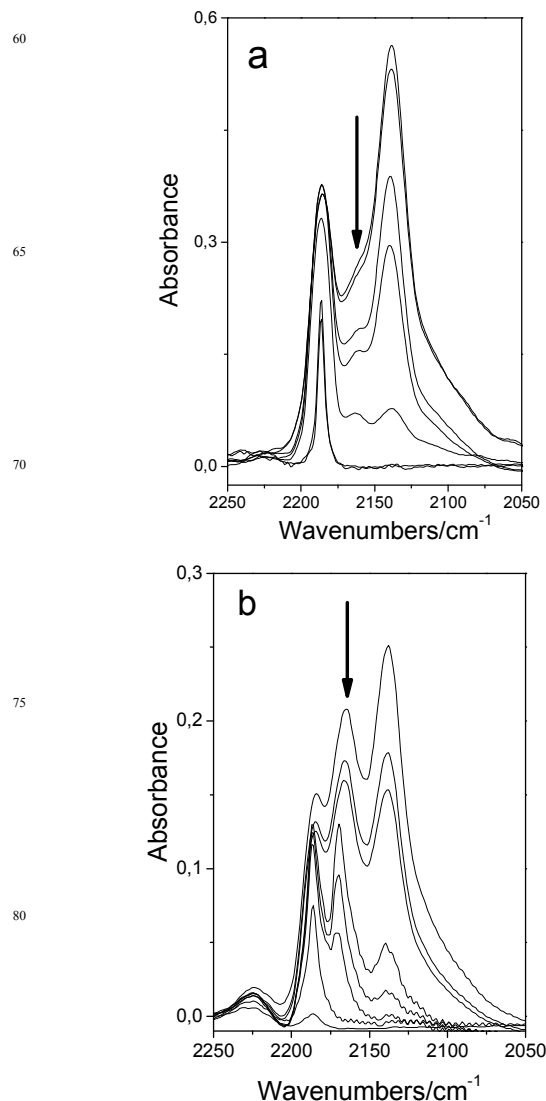
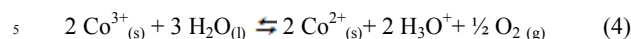


Figure 5. IR spectra in the CO stretching range ( $2250\text{--}2050\text{ cm}^{-1}$ ) obtained after dosing CO at nominal  $77\text{ K}$  on self-supporting wafers of calcined Co-APO-5 (a) and Co-APO-5 dried after reaction with water (b). CO equilibrium pressures in the  $0.50 - 30\text{ mbar}$  range.

### Mechanism of reaction

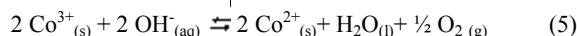
The need for a substantial presence of water, shown by the micro-calorimetric experiment in Figure 2, in order for the reaction to occur, is in our opinion the key to the understanding of the reaction. Catlow *et al.* have proposed that Co ions, when in the  $3+$  state and in tetrahedral coordination, change their coordinative state to octahedral upon exposure to polar molecules such as water.<sup>33</sup>  $\text{Co}^{3+}$  cations in the presence of water molecules probably assume a tetra-oxo-di-aquo configuration, not that far from hexa-aquo similar species. These are unstable in liquid water<sup>17</sup> and undergo a proton-assisted electron transfer if the solution is not acidic. Indeed, the present case looks very similar,

because the lowering in pH brought about by the hydronium species formation is enough to halt the reaction, which starts again by adding bases. This points to a version of equation (1) where equilibrium among reactants and products is established:



or to a mechanism where hydronium ions inhibit the reaction.

The possible oxidation of hydroxide ions taking place according to equation (5):



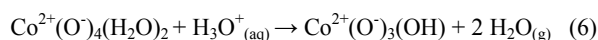
in our opinion should be ruled out, since the formation of 12  $\mu\text{mol}$  oxygen requires 48  $\mu\text{mol}$   $\text{OH}^{-}$ , but the starting solution had a pH of 5.6, corresponding to a  $[\text{OH}^{-}]$  of about  $4.0 \times 10^{-9}$  M that is  $8.0 \times 10^{-12}$  mol  $\text{OH}^{-}$  in 2.0 mL water.

The mechanism of reaction by which Co ions promote the oxidation of water is debated. It has to be noted at any rate that the present case is different from the cases referred to in the Introduction, where an electric bias is introduced so to promote the anodic oxidation of water, or a sacrificial reactant accepts electrons coming from the water oxidation. In those cases, it is well possible that high valence states of Co are involved. Here, the chemistry seems to be much straightforward, and to envisage only Co in the 2+ and 3+ valence states.

#### Thermal treatment of the sample after reaction

The sample after reaction with water underwent a TPD measurement, with simultaneous MS analysis of the evolved products (Figures 6a and 6b, respectively). TPD profile shows two mass losses, with maxima at about 393 and 520 K. MS shows that the mass loss at about 393 K is due to water desorption, whereas the latter at higher temperatures is due to hydrogen.

During the heating stage, two processes take place, i.e. dehydration and proton transfer (eq. 6):



followed by hydrogen evolution (7):

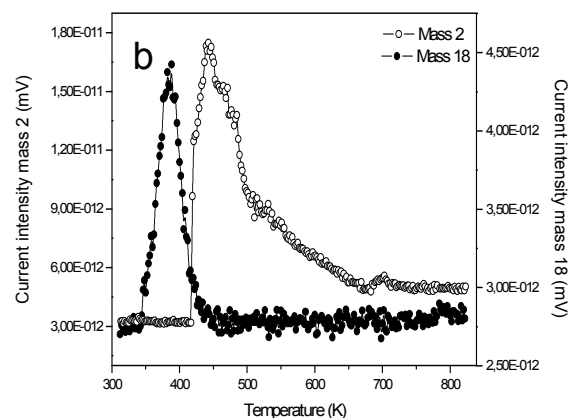
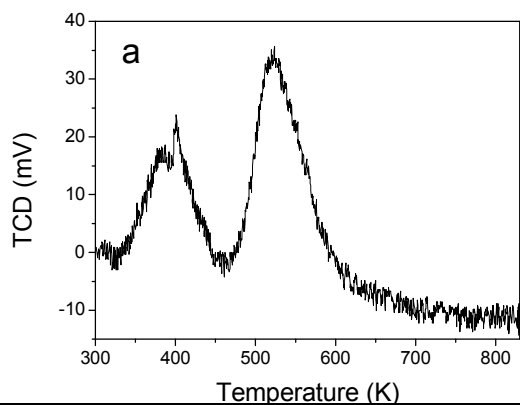
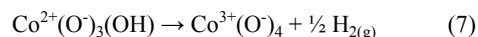
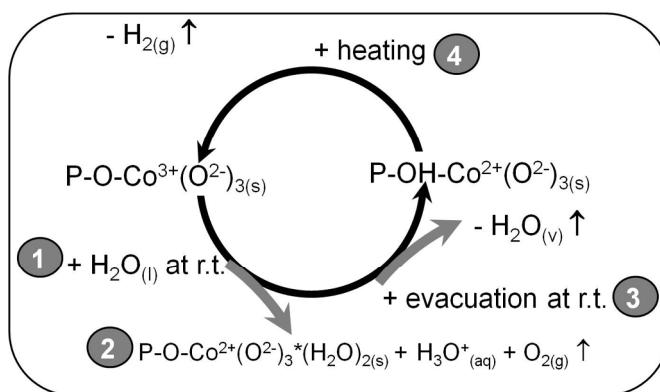


Figure 6. Temperature Programmed Desorption (TPD) profile of the sample after reaction with water (a); mass-spectrometry profiles of both mass 18 (black symbols) and mass 2 (hollow symbols) fragments (b).

The fact that thermal treatment brings the Co ions back to the 3+ tetrahedral configuration is confirmed by DR UV-Vis measurements, which yield spectra similar to curve (b) in Figure 1.

In conclusion, because heating of the sample leads to the release of hydrogen, the sum of equation (1) and (7) is nothing but the splitting of water, obtained under relatively mild thermal conditions. This is a result of some interest, both from the purely chemical point of view and possibly also from a practical one.<sup>43</sup> Indeed, a catalytic thermal cycle can be conceived, as depicted in Scheme 3, whereby alternating wet and dry conditions leads to WS.



Scheme 3. Catalytic thermal cycle for the WS by Co-APO-5.

Several thermodynamic cycles for the WS reaction have been proposed in the past. A most quoted review is that by Chao,<sup>46</sup> basically dealing with catalytic systems operating between two temperatures, a high one ( $T_H$ ) at which absorption of heat ( $Q$ ) occurs, and a lower one ( $T_L$ ) at which excess heat is released.



Under these circumstances, the theoretical efficiency requires that:

$$Q[1-T_H/T_L] \geq \Delta G(H_2O) \quad (8)$$

Kasai and Bishop<sup>47</sup> have discussed in these terms the possible use of transition-metal substituted zeolites in a paper that bears much resemblance with the present one. The interesting feature of the cycle in Scheme 3 is that both the step at high and low temperatures are endothermic, so that the limitations expressed by eq. 8 do not apply. Moreover, the range of temperature involved is definitely more moderate than the cases discussed by Chao. To check whether the cycle in Scheme 3 is practically feasible, the same sample was contacted with liquid water and then outgassed for five times. The evolution of Oxygen in the former step, and of Hydrogen in the latter was always observed, with apparently no big loss in the chemical activity. It seems therefore possible to carry out a cyclic process employing Co-APO-5 by using thermal energy only, under conditions very mild with respect to similar processes.<sup>48</sup> Co-APO-5 framework stability to cycling was tested by X-rays powder diffraction: Figure 7 compares XRD patterns of the sample calcined and after 5 cycles, showing. Both XRD patterns show only the typical peaks of the expected AFI structure.<sup>19</sup> No new peaks were observed after reaction.

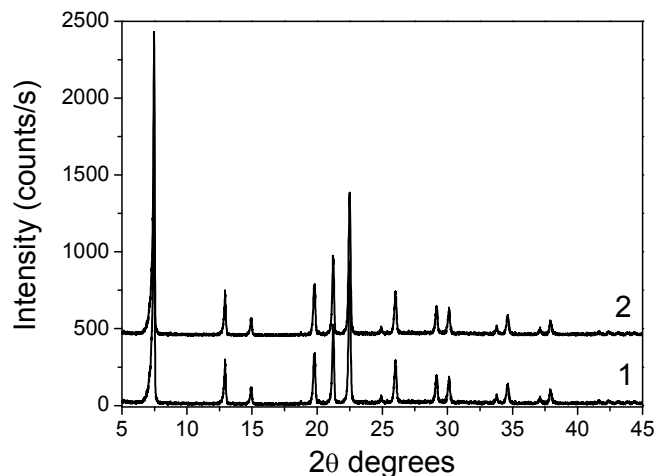


Figure 7. XRD patterns of calcined Co-APO-5 (1) and of Co-APO-5 after five reaction cycles.

## Conclusions

Reaction of Co-APO-5 with liquid water at room temperature was observed, because tetrahedrally coordinated  $\text{Co}^{3+}$  sites substituting for  $\text{Al}^{3+}$  in the aluminophosphate framework are able to oxidise liquid water at room temperature, by forming gaseous oxygen and protons that are released to the water suspension. A possible reaction mechanism is proposed, whereby Co cobalt (III) sites in aqueous suspension coordinate two water molecules, so becoming octahedrally coordinated and therefore unstable, as is the case for aquo-coordinated  $\text{Co}^{3+}$  cations in water. Oxidation of water was so observed without the need for either light, electrical power or sacrificial reagents.

Cobalt(III) sites are reduced to Co(II) sites: the latter may be re-oxidized by release of gaseous hydrogen by heating at only ca. 520 K. A definition of the configuration of the active site is outside the scope of this work, one reason being that the location of Co ions in the APO structure may be not random, and clusters may occur. It has however to be noted that both UV-Vis and XPS spectroscopies indicate that only a fraction (ca. 19%) of  $\text{Co}^{3+}$  sites is active.

Separate studies have shown that the same Co-APO-5 system is active in two closely related processes: i) the photo-oxidation of water in an electrochemical cell;<sup>31</sup> ii) in the absence of any electrical bias, but in the presence of a sensitizer and a sacrificial reagent.<sup>30</sup> The present study strongly suggest that the Co species active in either electrochemical or dye-promoted reactions are probably the same able to undergo the change in valence state documented in the present study.

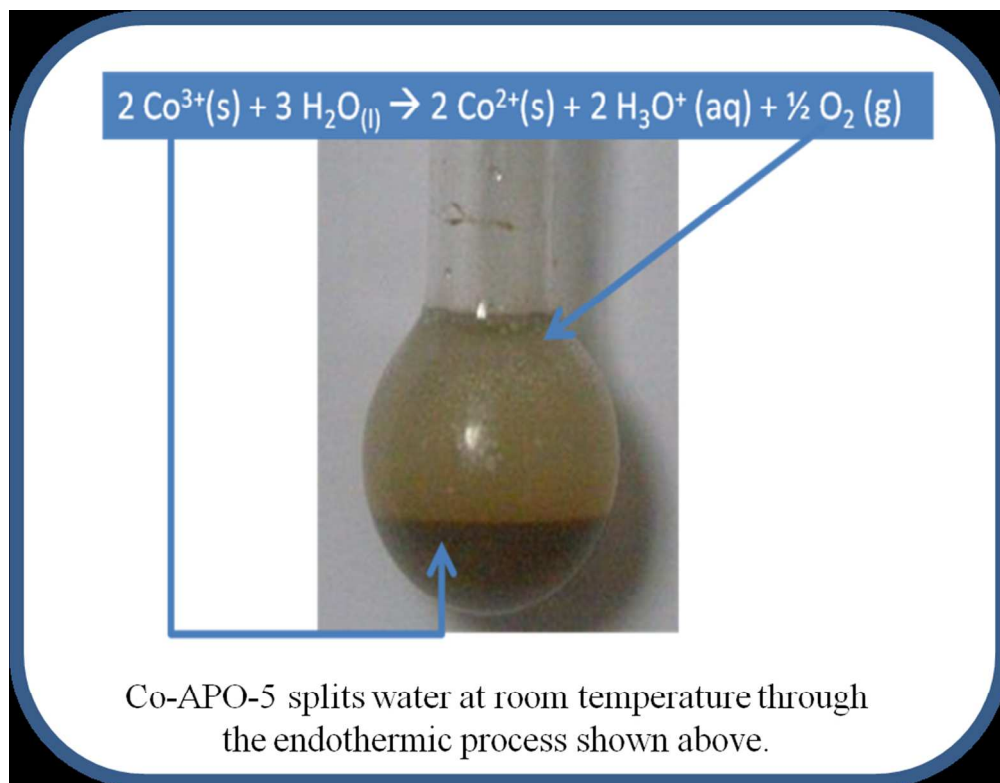
## Acknowledgements

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