

Supporting information

Cobalt-containing layered or zeolitic silicates as photocatalysts for hydrogen generation

*Ștefan Neațu, Marta Puche, Vicente Fornés, and Hermenegildo Garcia**

Instituto Universitario de Tecnología Química CSIC-UPV, Politecnica de Valencia, Avda. de los Naranjos s/n, 46022, Valencia, Spain. E-mail: hgarcia@quim.upv.es

1. Experimental Section

1.1. Materials

SiO₂ in form of colloidal suspension in water (Ludox AS-40), alumina and Co(CH₃COO)₂ • 4H₂O have been purchased from Sigma-Aldrich. NaOH (99.99 %) has been provided by Scharlau, while trans-4-aminocyclohexanol (97 %) has been purchased from Across. All reagents have been used as received without further purification.

Synthesis of Co-magadiite

The synthesis of Co-containing magadiite (Co-magadiite) was performed following a procedure already reported in ref. [1]. The synthesis was carried out under hydrothermal conditions in basic medium in the presence of a structure-directing agent, which in this case is trans-4-aminocyclohexanol. Briefly, the synthesis gel has been obtained by mixing the components in the following molar ratio: SiO₂/0.2 NaOH/0.5 trans-4-aminocyclohexanol/15 H₂O/0.02 Co(OAC)₂. The mixture is well stirred for 5 h and then transferred into a Teflon-lined autoclave and heated at 150 °C for 36 h. The obtained solid was exhaustively washed with deionized water and dried at 100 °C for 12 h.

Synthesis of [Co]Y

The synthesis of [Co]Y was carried out as disclosed in the patent literature [2]. Briefly, the synthesis consists in two steps. In the first one, seeds of zeolite Y not containing Co are prepared. In the second step, this zeolite Y seeds are grown using Co-containing magadiite as supplementary source of silicon. Preparation of zeolite Y seeds was carried out at room temperature dissolving 3.12 g of alumina Al₂O₃ in 38.70 g of MilliQ water using 12.78 g of sodium hydroxide and adding to this solution 25 g of SiO₂. The mixture is vigorously stirred at 350 rpm for 45 min and is allowed to age for 1 day at room temperature. In the second step, 3.73 g of zeolite Y seeds are added to an aqueous solution containing 38.065 g of water, 1.745 g of NaOH and 1.246 g of NaAlO₂ plus 10 g of Co-magadiite. The mixture was stirred for 1 h at 350 rpm and, then, the gel transferred to a polypropylene flask that was heated at 100 °C in static conditions for 24 h. The solid was collected, exhaustively washed and dried at 100 °C.

Synthesis of [CoO]Y

[CoO]Y was obtained by calcination of the [Co]Y at 540 °C for 8 h under air.

1.2. Photocatalyst characterization

The samples have been investigated using different characterization techniques like UV-Vis spectroscopy in diffuse reflectance mode, powder X-ray diffraction, temperature programmed reduction analysis, thermogravimetric, chemical and textural analysis, scanning and transmission electron microscopy. Diffuse reflectance spectra (DRS) in the range of 200–800 nm were recorded on a Cary 5 Varian spectrophotometer equipped with a Praying Mantis (Harrick) diffuse reflectance accessory. The computer processing of the spectra permits calculation of the Kubelka–Munk function $F(R)$ from the absorbance. All spectra were obtained under ambient conditions. Powder X-ray diffraction (XRD) patterns were recorded on a Philips X'Pert PW3719 diffractometer with Bragg-Brentano geometry, equipped with a graphite polarizer and autosampler, which used the Cu $K\alpha$ radiation (wavelength 1.54184 Å) and an excitation potential of 2 kW. The patterns were collected ranging 2θ from 1 to 40° with an angular speed of the goniometer of 0.02 2 θ /s. The adsorption measurements were performed using a Micromeritics ASAP 2000 sorption analyzer. Surface areas have been obtained by N₂ adsorption at the nominal temperature of liquid nitrogen (~77 K) on all materials previously outgassed at 673 K in vacuum. The specific surface areas and the pore size distributions were calculated from the Brunauer–Emmett–Teller (BET) equation³ and from the desorption isotherm using the Horvath-Kawazoe method,⁴ respectively. The temperature programmed reduction analyses (TPR) have been executed on TPD-TPR Micromeritics 2910 analyzer equipped with a TCD detector working at high temperatures. Approximately 100 mg of solid sample previously pretreated in Ar for 30 min have been introduced in the equipment quartz reactor and heated up to 950 °C with a heating velocity of 10 °C/min in a constant flow (50 mL/min) of hydrogen (15 vol. % H₂ in Ar). For the thermogravimetric analysis of the solid samples, a Mettler Toledo TGA/SDTA 851e thermal analyzer equipped with Al₂O₃ crucible and S-type thermocouple (Rh-Pt, 10 % Pt) has been used. Small quantities of solid samples (from 2 to 10 mg) have been heated from 20 until 800 °C with a heating velocity of 10 °C/min in a flow of dried-air (30 mL/min). The chemical analysis of the samples has been performed using an ICP-OES spectrophotometer from Varian. The solid samples (~50 mg) have been dispersed in a mixture (2 mL 1:1 volumetric ratio) of HF (48 %) and HNO₃ (60 %) and, after complete dissolution, MilliQ water is added (until 50 mL total volume). To establish the presence of any organic material in the samples, the materials were also characterized by combustion elemental analysis using an EA-1108 CHN-S analyzer from Fisons with sulfanilamide as standard. The scanning electron microscopy measurements have been performed on a JEOL 6300 SEM microscope equipped with a system of energy dispersive microanalysis Oxford Instruments Link–Isis, while the TEM measurements have implied the use of a CM 10 microscope from Philips working at 100 kV accelerating voltage.

The main objective of the characterization was to show that the incorporated cobalt cations are located in the framework of the silicate replacing silicon. In the case of Co-magadiite material, to discard the possible presence of extraframework cobalt, another type of material has been prepared by incorporation of Co (in the same amount, i.e. 2.4 wt. %) into the matrix following an ion-exchange procedure with cobalt acetate (the same salt used in the synthesis). Using UV-Vis spectroscopy we were able to determine the oxidation state and the coordination of cobalt. Figures S1 and S2 present the spectra of the cobalt containing materials used in this study. As it can be observed, besides the band at around 220-250 nm corresponding to the charge transfer Co²⁺–O,⁵ and the band at 350 nm attributed to Co in trigonal coordination,⁶ the spectra of [Co]Y material possess a series of bands centered between 500 and 650 nm (see Figure S2-room temperature spectrum). This characteristic triplet is typical to the d-d transitions of Co²⁺ possessing a tetrahedral coordination (Td).⁷ Although these bands appears to be weak in the case of

[Co]Y zeolite, after gradual increase of the temperature till 540 °C (corresponding to the formation of [CoO]Y), the *in situ* UV-Vis spectra (Figure S2) revealed more clearly the characteristic triplet of Co²⁺ (Td). This growth of the Td bands is an indirect evidence that Co was present in the zeolite framework, before the calcination.

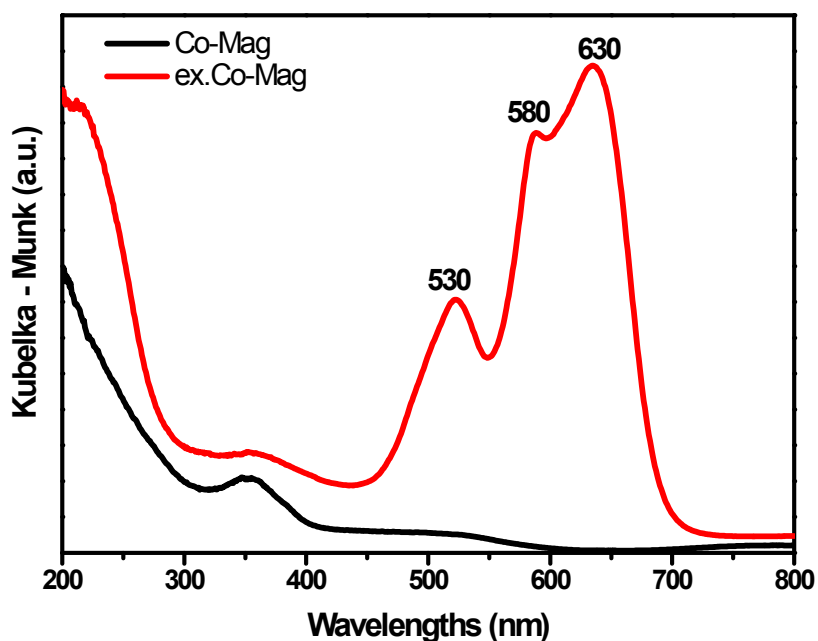


Figure S1. The DR-UV-Vis spectra of cobalt containing magadiite materials at the same Co loading prepared in two different ways. It can be observed that the exchanged magadiite (red spectrum), presents the characteristic triplet band at 530, 580 and 630 nm corresponding to Co²⁺ Td.

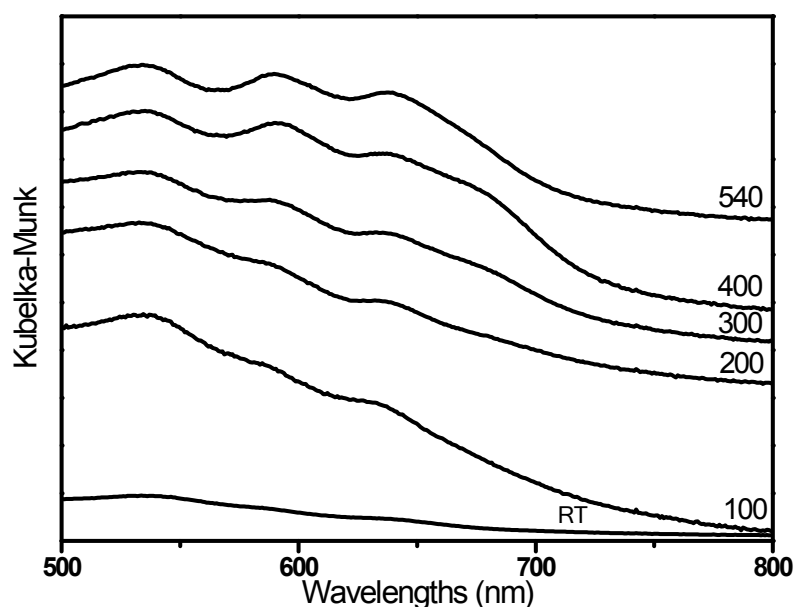


Figure S2. The DR-UV-Vis spectra of [Co]Y at different temperatures (from room temperature until 540 °C) collected by using the Praying Mantis diffuse reflectance accessory. For clarity, just the region 500-800 nm of the spectra is presented.

Figure S3 corresponds to the X-ray patterns of the Co-magadiite and the exchanged magadiite. Two facts are observed: the sample has less exchanged interlaminar distance (1.21 nm) and a lower crystallinity while Co-magadiite possesses a 1.55 nm interlaminar distance and a high crystallinity.

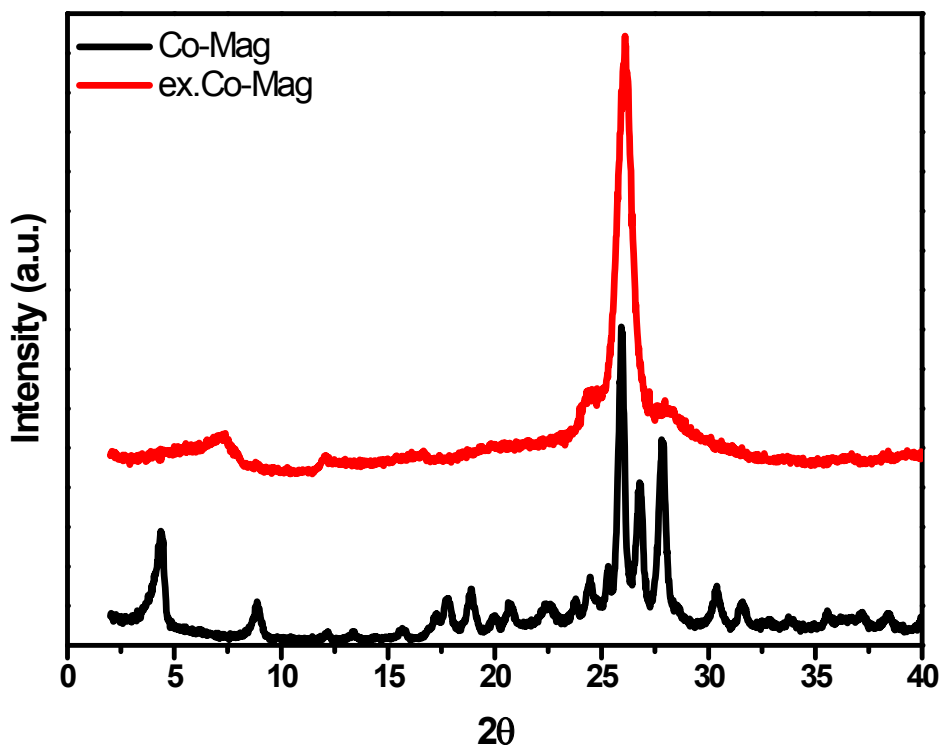


Figure S3. XRD patterns of Co-magadiite and exchanged magadiite materials.

To prove the incorporation of Co in the framework of zeolite Y, both Co-magadiite and [Co]Y samples have been treated with a solution of sodium chloride in water (2.5 M) and refluxed at 80 °C for several hours. The analysis of both solution and filtrated material revealed that no cobalt is detected in the solution while the solid sample presents the same value as before the treatment. Although we could suppose that the substitution of silicon by cobalt is not isomorphous due to the differences in the radius and the charges of both metal ions (Co^{2+} has a radius of 0.074 nm, while in the case of Si^{4+} is 0.041 nm), it can be assumed that the incorporation of cobalt within the framework must cause deformation thereof creating structural defects.

To determine the oxidation/reduction ability of cobalt atoms within the framework of [Co]Y zeolite, a TPR study of this material has been performed. Figure S4 presents the TPR profiles of (a) the original [Co]Y and (b) the previously oxidized sample (400 °C in oxygen). According to the literature, the CoO is reduced at temperatures below 500 °C⁷ when the interaction surface is very low (large crystals) and above 750 °C⁸ when the interaction is very strong (very small crystals). Furthermore, Co^{3+} oxide (Co_3O_4) is reduced at lower temperatures, around 370 °C.⁹ Finally, Co^{2+} cations in exchange positions are reduced with greater difficulty, depending on the zeolite at temperatures between 450 and 1100 °C.⁹ Nevertheless, and given that, as we have shown that [Co]Y has no metal cations in exchange positions, the spectrum shown in Figure S4 (a) indicates that the built-in framework [Co]Y zeolite is reduced to a temperature of around 650 °C, which does not match either of the above cases. The measurement of H_2 consumed during reduction allows us to determine the amount of Co^{2+} is 2.3 wt. % cobalt, with the amount matching the

value already measured by chemical elemental analysis, which is 2.4 wt. %. This result allows us to conclude that the reduction of cobalt in the network of the zeolite is 100%. The TPR spectrum of previously oxidized sample, Figure S4 (b), clearly indicates that only part of initial Co^{2+} is able to be oxidized to Co_3O_4 , which is the compound responsible for the reduction profile appearing around 390 °C in the spectrum TPR. To summarize, the TPR analysis the [Co]Y zeolite confirms the presence of fully reduced cobalt within the framework, a part of which may undergo redox processes.

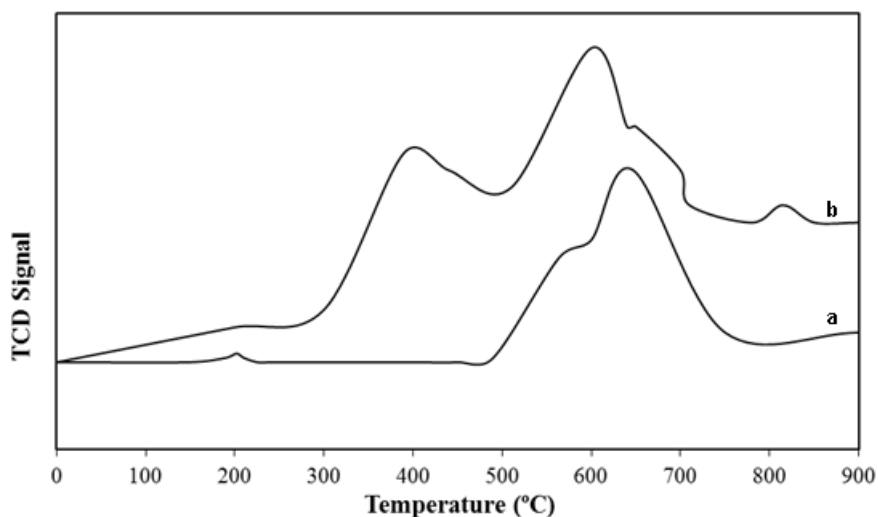


Figure S4. The TPR profiles of (a) the original unoxidized, and (b) the previously oxidized [Co]Y sample.

All characterization results described so far (DR-UV-Vis, XRD and TPR) for the zeolite Y containing cobalt indicate that Co occupies very likely lattice positions.

The layered nature of the Co-magadiite material can easily be observed in the Figure S5, in which a representative image of this material is presented. No other Co-containing particles formation could microscopically be observed.

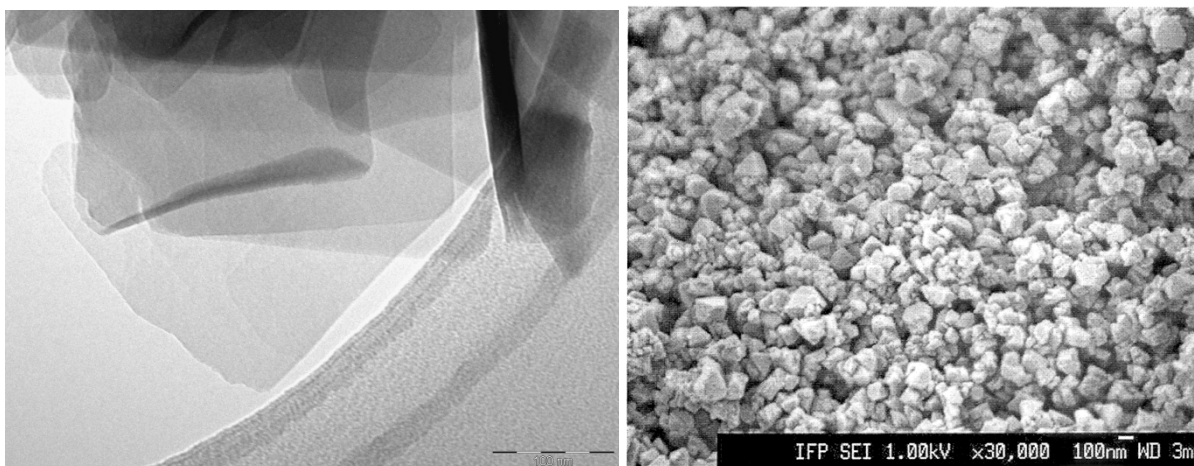


Figure S5. TEM (left) and SEM (right) images of the Co-magadiite material.

The Figure S6 shows a representative TEM image of [Co]Y material. As it can be observed no extraframework cobalt species could be visualized, indicating that most of the cobalt is located inside the framework of the zeolite Y material.

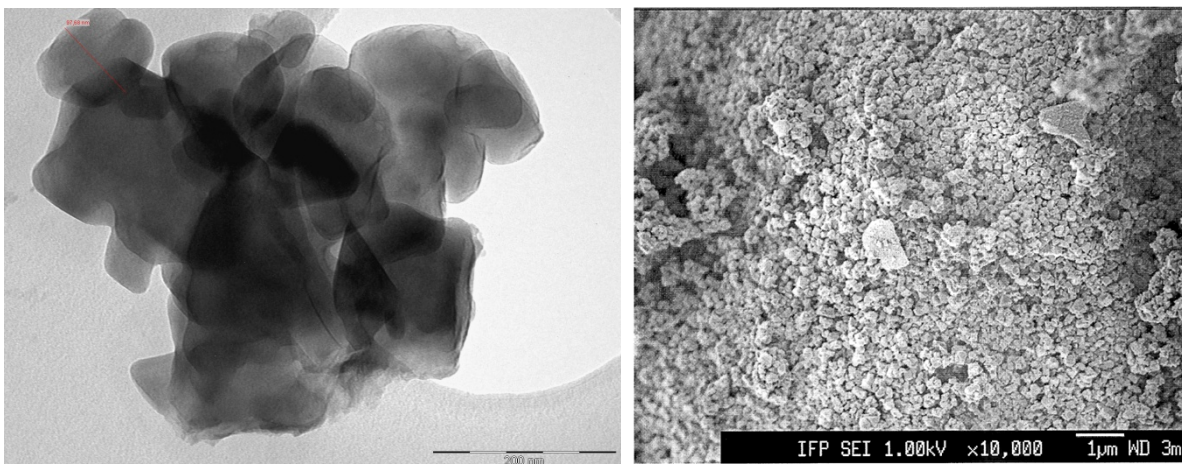


Figure S6. TEM (left) and SEM (right) images of the [Co]Y material.

In contrast to the previous observation, the TEM micrographs [CoO]Y obtained by calcination of the [Co]Y at 540 °C in air (Figure S7) shows the presence of large cobalt oxide particles with sizes of ca. 40 nm. These particles appear to be formed by the migration of the small cobalt oxide particles outside the framework of the zeolite Y when high calcination temperature has been applied.

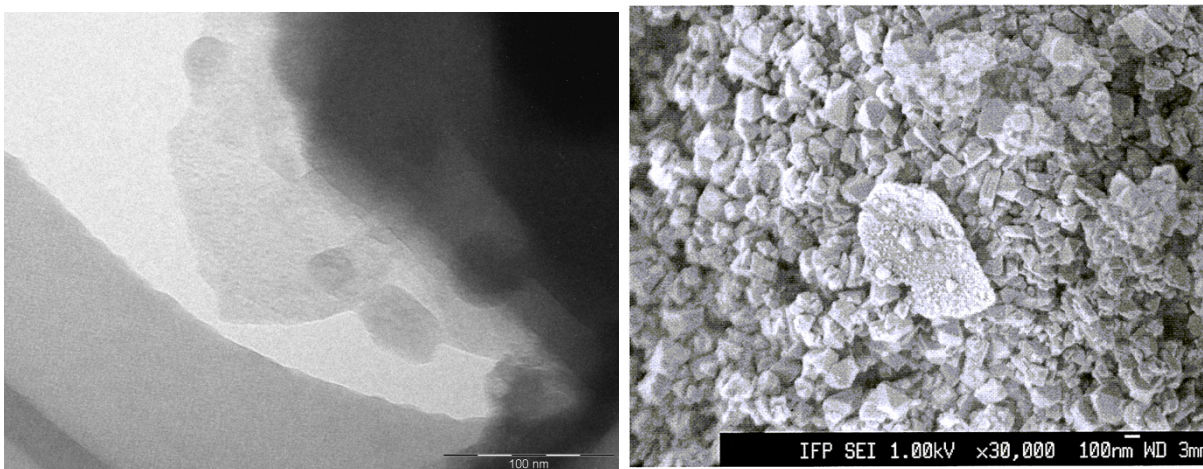


Figure S7. TEM (left) and SEM (right) images of the [CoO]Y material.

The extended X-ray absorption fine structure (EXAFS) measurements (Co K-edge) on our samples have been also carried out to determine the structure and the electronic state of the cobalt species present in the samples. As can be observed from the data presented in Figure S8, [Co]Y presents octahedral Co^{2+} , while exposing this material to a heating treatment at 540 °C, leading to the formation of [CoO]Y, a transition to tetrahedral Co^{2+} appears to take place.

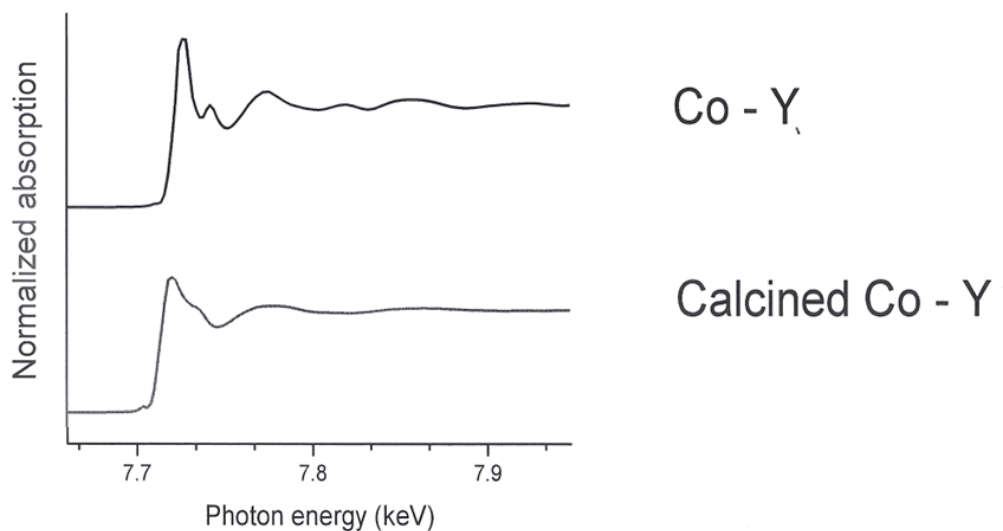


Figure S8. The X-ray absorption spectrum of the Co K edge for the [Co]Y and [CoO]Y samples.

1.3. Photocatalytic reactions

In a typical experiment, 25 mg of photocatalytic powder was added to 25 mL of deionized water or of a H₂O:CH₃OH mixture (4:1 volumetric ratio) and dispersed by sonication for 15 min. The resulting slurry was then transferred to a cylindrical quartz reactor and purged with argon (5 mL min⁻¹). The internal volume of the quartz reactor was around 55 mL. The reactor was equipped with two gas valves one for inlet and the other for outlet to which a pressure gauge was attached. After purging for at least 30 min, the reactor was pressurized and depressurized to 1.4 bar for five cycles and finally loaded with argon (1.4 bar) and closed. The suspension was stirred (500 min⁻¹) and irradiated with either a medium pressure Hg lamp or a solar simulator (only suspensions containing H₂O:CH₃OH mixture). In both cases the quartz reactor was immersed in water bath working at around 25 °C while the irradiation has been performed only from the top. In the case of the Hg lamp (125 W), irradiation was performed at a distance of ca. 6 cm between the light source and the suspension surface for 12 h. In experiments where simulated solar light (Oriel Solar Simulator with a 1000 W xenon lamp coupled with an AM1.5 filter that provides simulated concentrated sunlight) was used, the suspension was illuminated with a collimated light beam at a distance of ca. 10 cm for 12 h. The emission spectra of both irradiation sources are presented in Figure S9. After the light had been switched off, the suspension was kept under stirring until the pressure inside the reactor had stabilised. The gaseous samples were taken through the outlet valve port with a Hamilton syringe (100 μL) and injected “on-column” into a gas chromatograph (Agilent Technologies 7890A GC System) equipped with a Molecular Sieve 5 column (carrier gas: Ar, flow = 5 mL min⁻¹) and a thermal conductivity detector (TCD) for the quantification of H₂. The photocatalytic activity of the samples has been expressed as number of micromoles of H₂ formed per gram of Co per hour. We have to note that no sacrificial reagent was used in the water splitting experiments performed under UV irradiation. In order to compare the photoactivity of our samples with that of CoO, several experiments comprising the use of commercially available cobalt oxide (purchasing from Sigma Aldrich) have also been performed. No hydrogen or oxygen generation has been detected under our experimental conditions. Besides that, several blank experiments (with no catalyst) has been performed in order to prove that the hydrogen production come only from the water splitting process. Since in the case of the experiments performed under UV radiation there were no generation of hydrogen (or below the GC detection limit), when the simulated

solar light was used hydrogen production was detected but in a negligible amount respect to the photocatalytic tests.

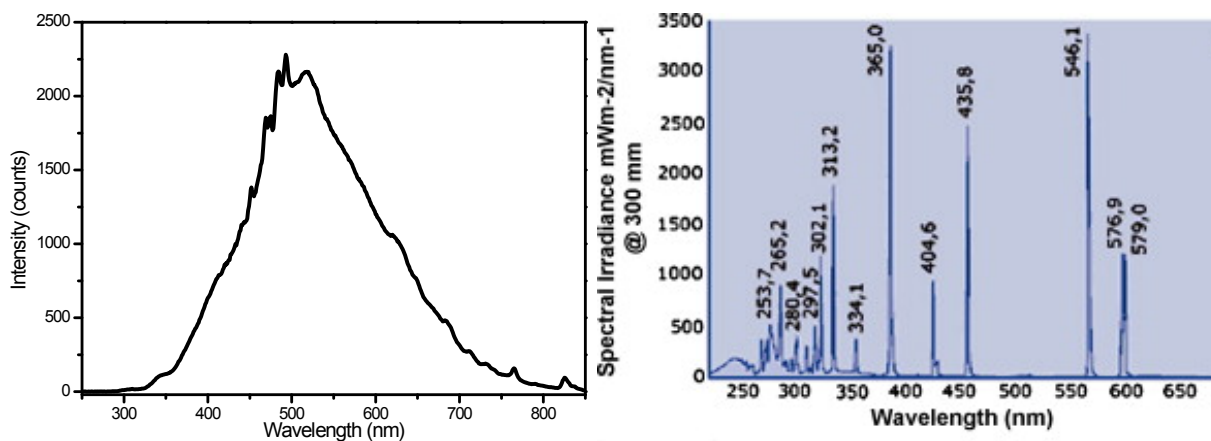


Figure S9. The emission spectra of the irradiation sources used in this work: 1000 W Xe lamp (left) and 125 W Hg lamp (right).

2. References:

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