

Effect of cobalt hydroxo-sulphide on organic material radiolysis

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Abstract

In the context of nuclear waste management, the release of hydrogen can generate safety problems. It has been shown that amorphous cobalt hydroxo-sulphide is able to decrease the apparent production of radiolytic hydrogen yield by hydrocarbon radiolysis. This paper presents a study of the effect of cobalt hydroxo-sulfide on the radiolysis of propane induced by a proton beam. Hydrogen and hydrocarbon partial pressures obtained after propane irradiation were compared in different conditions: (i) without cobalt hydroxo-sulphide, (ii) in the presence of solid, irradiated or not, by adjusting the gas pressure in the irradiation cell. The evolution of those partial pressures as a function of the time of contact between the amorphous cobalt hydroxo-sulphide and the formed gaseous species is discussed. The solid is characterised by X-ray diffraction, infra-red and Raman spectroscopies before and after hydrogen trapping. It is shown that the solid does not change the composition and amount of organic radiolytic products but acts as a trap of hydrogen. The hydrogen consumption by the solid seems to be proportional to the initial hydrogen partial pressure. This study shows that radiolytic hydrogen is rapidly produced by propane irradiation whereas the trapping of hydrogen by cobalt hydroxo-sulphide is a slower phenomenon.

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1. Introduction

In France, some radioactive wastes (containing α , β , γ radioactivity) resulting from the reprocessing

of irradiated fuels are embedded in bitumen. The self-irradiation of the bituminised waste leads mainly to the production of radiolytic hydrogen (75–95 vol.% of produced radiolytic gas) [1]. It has been shown that the presence in the barrels of cobalt hydroxo-sulphide reduces considerably the production of hydrogen [2] but no scientific explanation of the phenomenon was established. In the present work, the effect of cobalt hydroxo-sulphide on the radiolytic hydrogen release was studied.

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This paper presents a fundamental study of the effect of cobalt hydroxo-sulphide on the radiolysis of propane induced by a proton beam. The bitumen, which are complex molecules, were modelled as simple organic molecules: our choice was directed towards gaseous propane (the reason of this choice is explained on the next section). The alpha activity constituting the most efficient radiation in terms of radiolytic gas production oriented the focus of this work. Charged particles are simulated by protons; their amount is negligible versus the hydrogen produced by radiolysis.

2. Experimental

2.1. Extracted beam line and irradiation cell

The irradiation experiments were performed with a 3.0 MeV energy proton beam at the Van de Graaff accelerator of the 'Institut de Physique Nucléaire de Lyon'. The choice of irradiated gas is explained by the fact that the proton linear energy transfer (LET) is lower in gases than in liquids or solids. The proton range is thus greater in gas than in liquid medium.

The specific extracted beam line, associated to a gas irradiation cell, has been set up on the 4 MV facility of the IPNL. The characteristics of this extracted beam line and analysis conditions of irradiated gases are described in detail in a previous work [3]. The studied system is irradiated at room temperature with a dose rate of 50 MGy h^{-1} , the total irradiation doses applied being in the range of 0.6–3.6 MGy. Hydrogen and hydrocarbon productions were analysed by a gas chromatography device directly coupled with the irradiation cell. Cobalt hydroxo-sulphide stacked pellets of 150 mg were fixed at the bottom of the irradiation cell. As a function of the proton mean path length, either both gaseous hydrocarbons and the solid were simultaneously irradiated (for pressures of 35 kPa), or only hydrocarbons were irradiated (for pressures of 100 kPa). These experimental conditions enabled us to study the influence of the solid irradiation on the inhibition of hydrogen production.

2.2. Gas nature and cobalt hydroxo-sulphide synthesis

In this study propane has used as alkanes which were Messer research grade (purity = 99.95%). The amorphous cobalt hydroxo-sulphide was obtained

by precipitation of aqueous cobalt nitrate (0.1 M) with aqueous sodium sulphide (0.1 M) followed by filtration, thorough washing and drying in inert atmosphere [4].

2.3. Characterisations of the solid

Transmission electron micrographs were obtained on a JEOL 2010 electron microscope with a LaB_6 filament as the source of electrons, operated at 200 kV. The X-ray diffraction patterns were obtained on a Siemens D5000 diffractometer with $\text{Cu K}\alpha$ emission. The diffractograms were analysed using the standard JCPDS files. The ATR FT-IR spectra were acquired in the $400\text{--}4000 \text{ cm}^{-1}$ wavenumber range, on a BIORAD FT-IR interferometer and with the use of 32 scans and a nominal resolution of 4 cm^{-1} . The cobalt hydroxo-sulphide was mixed with to KBr at 9%, w/w. The same procedure was used for scanning blank spectra of KBr alone. XRD and Infra-red analysis were performed at the Ecole des Mines de Saint Etienne. Raman spectra were obtained on a Raman Renishaw RM1000 microspectrometer device at the 514 nm light wavelength, using a laser power of 2 mW and a spectral resolution of 4 cm^{-1} . These experiments were performed at the 'Laboratoire de Physico-Chimie des Matériaux Luminescents' of Lyon Claude Bernard University.

3. Results and discussion

3.1. Characterisation of the initial solid

The amorphous cobalt hydroxo-sulphide was obtained by reaction, at room temperature, between hydrated sodium sulphide dissolved in water and a hydrated nitrate cobalt salt. A black powder in suspension in water was immediately formed upon addition of Na_2S . This suspension was washed five times with large amounts of distilled water, filtered and dried in inert atmosphere (N_2). The solid obtained is unstable in air and even pyrophoric when fresh [5] and it is not a well-known compound. Because of the cobalt hydroxo-sulphide instability in contact with air, this solid was stored under nitrogen.

Powder X-ray diffraction (Fig. 1(a)) shows that the product is amorphous with some cobalt hydroxide impurities. Cobalt hydroxide might be formed due to hydrolysis of sulphide ions in aqueous solutions. Since for the reaction

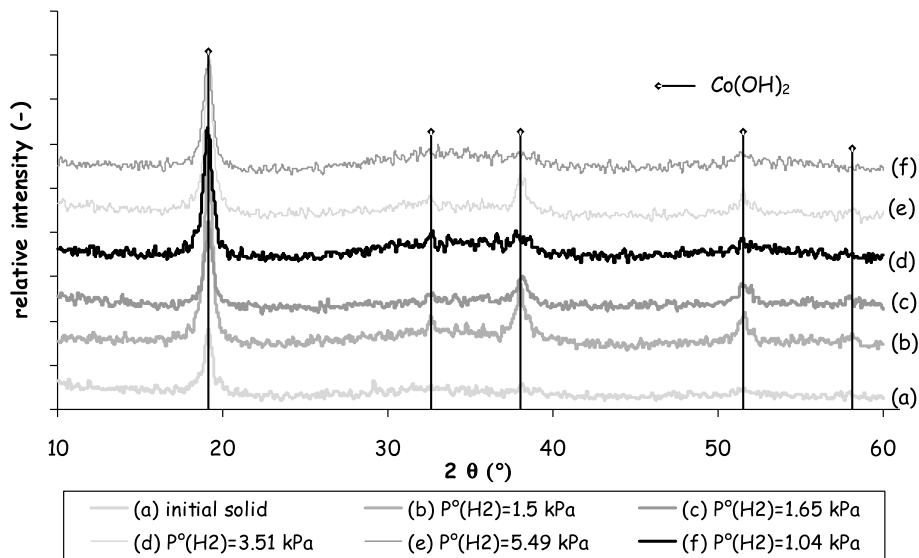
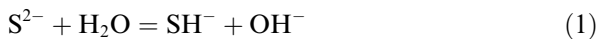


Fig. 1. XRD pattern of the initial cobalt hydroxo-sulphide (a) and after interaction with hydrogen at different pressures (b–f).



the equilibrium is completely shifted to the right side in a large pH range, considerable amounts of hydroxide are present in the Na_2S solutions. Due to basic pH of the solution, hydroxide precipitation seems possible as a side process. Nevertheless, according to the signal-to-noise ratio, the content of $\text{Co}(\text{OH})_2$ does not exceed some percents in our preparations.

Transmission electron microscopy of the initial solids reveals high dispersion of the amorphous matter where energy dispersed X-ray analysis gives a Co/S atomic ratio close to 1. In addition, rare inclusions of lamellar $\text{Co}(\text{OH})_2$ phase are present and the Co/S atomic ratio is equal to 5 (Fig. 2). Worth emphasizing that whatever the specimens, their main component is always amorphous cobalt hydroxo-sulphide.

Moreover, the analysis of the infrared spectra shown on Fig. 3(a), indicates the presence of water (large band between 3000 and 3600 cm^{-1} due to $\nu(\text{HO}-\text{H} \cdots \text{H})$ mode and band at 1645 cm^{-1} due to $\delta(\text{HOH})$ in water). The presence of bands at 3630 cm^{-1} (due to $\nu(\text{HO})$ mode), 1090 and 620 cm^{-1} (due to $\nu(\text{S}-\text{O})$ modes), reveals the presence of hydroxide and sulphates groups respectively. However, cobalt sulphate, unavoidable in this kind of materials, is not detected by XRD which means that CoSO_4 does not exceed some percents.

Complete chemical analysis (performed by the Service Central d'Analyse of CNRS) gives the fol-

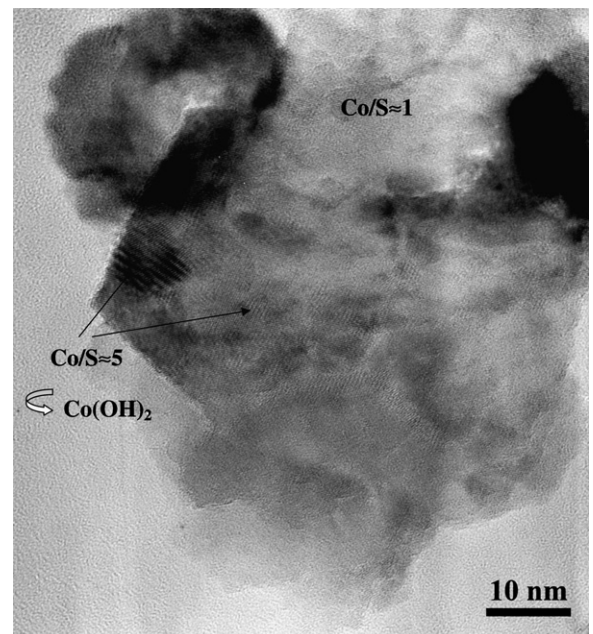


Fig. 2. Transmission microscopy image of cobalt hydroxo-sulphide initial solid representing an inclusion of lamellar $\text{Co}(\text{OH})_2$ crystallite in the amorphous matter of $\text{Co}_1\text{S}_x\text{O}_y\text{H}_z$.

lowing weight fractions of 43.9, 27.7, 24.8 and 1.4 on average for cobalt, sulphide, oxygen and hydrogen, respectively. The compositions of some solids $\text{Co}_1\text{S}_x\text{O}_y\text{H}_z$ after various syntheses are presented in Table 1. They show the variability of the solid composition.

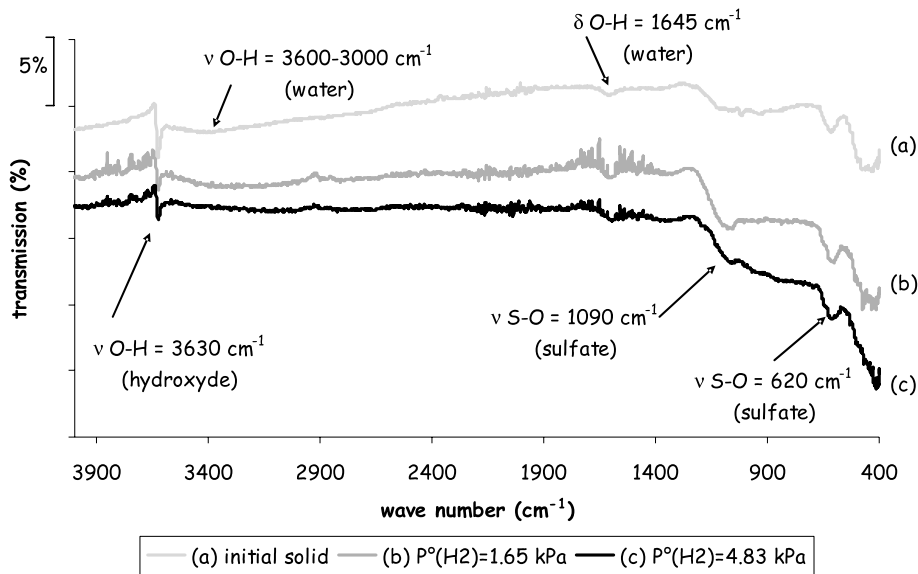


Fig. 3. Infrared spectra of the initial $\text{Co}_1\text{S}_x\text{O}_y\text{H}_z$ (a) and after interaction with hydrogen at various pressures (b and c).

Table 1

Compositions of some initial solids after precipitation, washing and drying

Sample	Co (at.%)	S (at.%)	O (at.%)	H (at.%)	$\text{Co}_1\text{S}_x\text{O}_y\text{H}_z$
1	19.2	20.6	33.0	27.1	$\text{Co}_1\text{S}_{1.1}\text{O}_{1.7}\text{H}_{1.4}$
2	21.6	22.1	33.3	23.0	$\text{Co}_1\text{S}_{1.0}\text{O}_{1.5}\text{H}_{1.1}$
3	17.3	20.0	38.6	24.1	$\text{Co}_1\text{S}_{1.2}\text{O}_{2.2}\text{H}_{1.4}$
4	21.9	24.0	33.4	20.6	$\text{Co}_1\text{S}_{1.1}\text{O}_{1.5}\text{H}_{0.9}$
5	13.0	16.3	36.4	34.4	$\text{Co}_1\text{S}_{1.3}\text{O}_{2.8}\text{H}_{2.6}$
6	15.0	18.3	37.9	28.8	$\text{Co}_1\text{S}_{1.2}\text{O}_{2.5}\text{H}_{1.9}$

3.2. Propane radiolysis

In a previous work [3], propane radiolysis induced by a proton beam has been studied. It has been shown that hydrogen and hydrocarbons (CH_4 , C_2H_4 , C_2H_6 , C_3H_6 , C_4H_8 , C_4H_{10} and higher hydrocarbons) were formed during irradiation of gaseous propane. Radiolysis of hydrocarbons occurs through formation of radical cations and their disappearance via ion-molecule reactions. Detailed radiolysis mechanisms can be found elsewhere [6,7]. The composition of the radiolysis prod-

ucts and particularly the radiolytic H_2 yield might be influenced (increased or decreased) by the presence of solids [8,9].

3.3. Effect of the cobalt hydroxo-sulphide on propane radiolysis

Propane was irradiated at a 0.6 MGy dose with an initial pressure of 100 kPa.

3.3.1. Immediately after irradiation

Under this propane initial pressure, cobalt hydroxo-sulphide is not irradiated. This 0.6 MGy irradiation dose allows the production about 1.1 kPa of radiolytic hydrogen.

The partial pressures of hydrogen and some hydrocarbons formed after irradiation of propane were compared with and without cobalt hydroxo-sulphide, immediately after irradiation, in Table 2. Those partial pressures are not modified by the presence of $\text{Co}_1\text{S}_x\text{O}_y\text{H}_z$ in the irradiation cell. Moreover, corresponding chromatograms revealed that the presence of the solid does not change the

Table 2

Partial pressures of hydrogen and hydrocarbons with and without cobalt hydroxo-sulphide

Partial pressures (kPa)	H_2	CH_4	C_2H_4	C_2H_6	C_4H_8	C_4H_{10}
Without solid	1.08 ± 0.13	0.25 ± 0.03	0.13 ± 0.02	0.46 ± 0.06	0.016 ± 0.002	0.071 ± 0.009
With solid	1.06 ± 0.13	0.23 ± 0.03	0.11 ± 0.01	0.43 ± 0.05	0.014 ± 0.002	0.073 ± 0.009

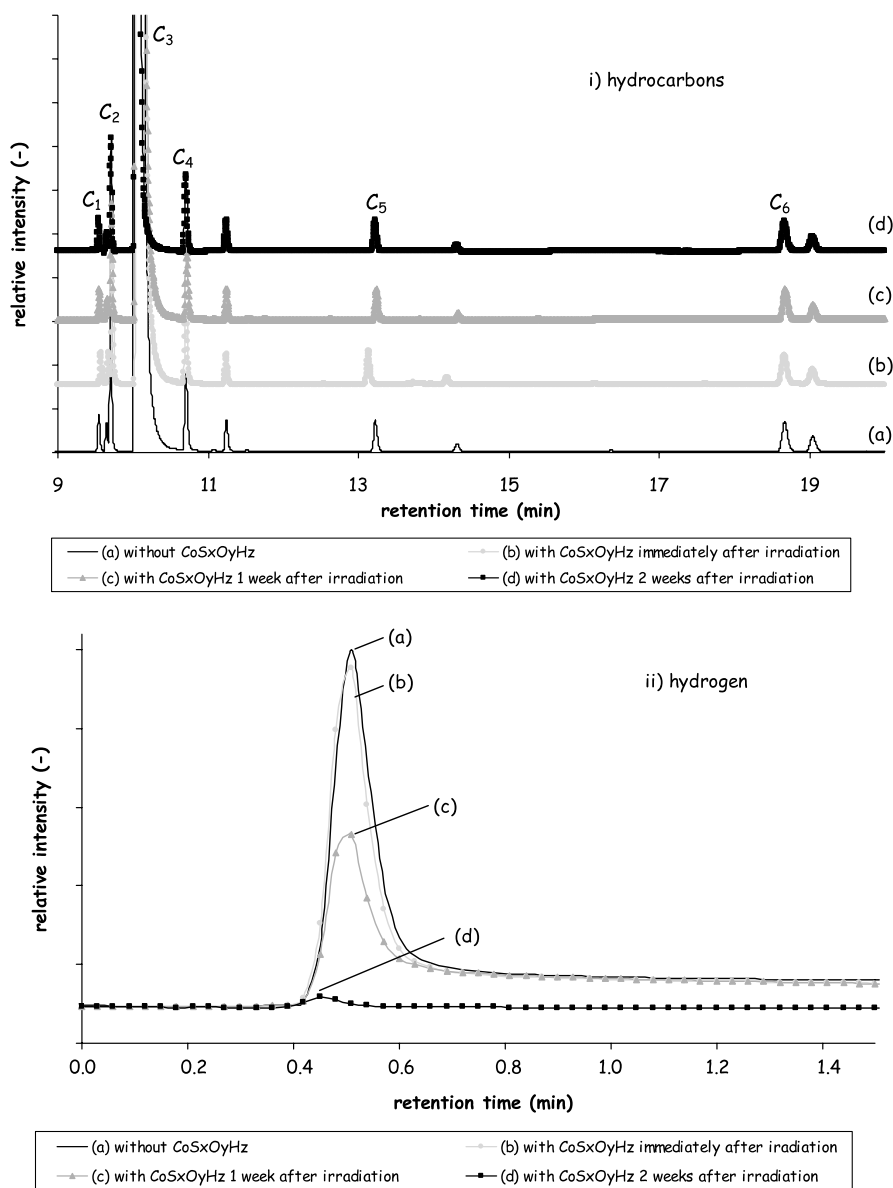


Fig. 4. Chromatograms obtained (i) for hydrocarbons, (ii) for hydrogen after various times of contact between irradiated gas and solid.

composition and the amount of organic radiolytic products (Fig. 4).

To reach, in the selected experimental conditions, a dose of 0.6 MGy, irradiated gaseous propane was carried out during about 30 min. Analysis of radiolysis products, realised immediately after irradiation by gas chromatography, requires about 45 min. It is known that the radical lifespan is about 10^{-5} second [6]. It can consequently be concluded that this solid does not act as a radical scavenger of species formed during irradiation. It was also observed that immediately after irradiation with cobalt hydroxo-sul-

phide, there was no reduction in the hydrogen apparent production. This means that the kinetics of inhibition of the hydrogen production by cobalt hydroxo-sulphide is a rather slow phenomenon. It was consequently decided to increase the time of contact between irradiated propane and the solid.

3.3.2. After various times of contact between irradiated gas and solid

In Fig. 4, hydrocarbons (i) and hydrogen (ii) chromatograms obtained by the analysis of gaseous

mixtures resulting of various contact times between irradiated gas and solid were compared.

The composition and the amount of hydrocarbons formed after propane radiolysis are exactly the same ones in presence or not of the solid and whatever the time of contact is. The hydrogenation products of carbon double bounds C=C were not detected and it was noticed that only hydrogen partial pressure has decreased. Moreover, after two weeks of contact there is almost no more hydrogen.

As a consequence, cobalt hydroxo-sulphide does not act as a catalyst of hydrogenation of unsaturated compounds but seems to be only a trap of hydrogen. The quantity of hydrogen fixed by the solid in these conditions was determined by the chromatogram comparison. It is equal to 0.013 mole of H₂ per mole of Co after four weeks of contact.

3.4. Solid irradiation effect on propane radiolysis

To observe the effect of the irradiation of the solid, it is necessary to compare the amount of hydrogen fixed by the solid, irradiated or not, for the same initial hydrogen partial pressure. At 100 kPa of propane, the solid is not irradiated and 1.1 kPa of radiolytic hydrogen is produced with a dose of 0.6 MGy. This same quantity of hydrogen is obtained with a 1.8 MGy dose when the solid is irradiated, that means for a propane pressure equal to 35 kPa.

Amounts of hydrogen fixed by cobalt hydroxo-sulphide after four weeks of contact between irradiated gaseous propane and solid are reported in Table 3. The amount of fixed hydrogen is the same if the solid has been irradiated or not, the mean value being approximately equal to 0.013 mole of H₂ per mole of Co.

For very low initial partial pressure of hydrogen, the irradiation of the solid does not modify the amount of fixed hydrogen. However this low hydrogen pressure could mask the effect of the irradiation of the solid. The influence of the hydrogen initial partial pressure on the capability of Co₁S_xO_yH_z to trap hydrogen was studied.

3.5. Hydrogen initial partial pressure effect

The variation of the irradiation dose of propane allows to modify the hydrogen initial partial pressure. So the applied total irradiation doses being in the range of 0.6–3.6 MGy, the pressure of produced radiolytic hydrogen extends to 0.35–5.5 kPa.

In Fig. 5, the amount of hydrogen stored by cobalt hydroxo-sulphide as a function of hydrogen initial partial pressure for a solid (irradiated or not) was plotted. It confirms that the amount of fixed hydrogen is not modified by the irradiation of the solid. Moreover, this amount is proportional to the hydrogen initial partial pressure.

Summarising the results presented above, it can be concluded that hydrogen trapping by the solid occurs independently on the propane radiolysis. Moreover, the proportionality between the amount of hydrogen stored by the cobalt hydroxo-sulphide and the initial hydrogen partial pressure is another argument in favour of the hydrogen sorption.

In order to better understand the hydrogen fixation mechanisms, the solid before and after interaction with hydrogen was characterised.

3.6. Characterisation of cobalt hydroxo-sulphide after hydrogen interaction

The initial cobalt hydroxo-sulphide and the solids that experienced various hydrogen pressures have been characterised by X-ray diffraction, infrared and Raman spectroscopies. The comparison between the various X-ray diffractograms (Fig. 1) shows that Co₁S_xO_yH_z remains unchanged whatever the hydrogen initial pressure is. All observed peaks correspond to the initially present Co(OH)₂ impurity phase. Note that the noise level is comparable to the peak intensity. Infrared spectrum (Fig. 3) reveals a slight decrease of the band characteristic to ν(O–H) mode of hydroxide (at 3630 cm⁻¹). In the Raman spectrum (Fig. 6) the formation of a new phase attributed to Co₉S₈ was clearly observed. It can be therefore concluded that a chemical reaction has occurred.

Table 3

Amounts of hydrogen fixed by cobalt hydroxo-sulphide after 4 weeks of contact between irradiated gaseous propane and solid

	Initial P_{H_2} (kPa)	Final P_{H_2} (kPa)	Molar fraction of H ₂ fixed per Co solid (–)
Irradiated solid	1.02 ± 0.12	0.079 ± 0.009	0.0123 ± 0.0015
Non irradiated solid	1.08 ± 0.13	0.035 ± 0.004	0.0135 ± 0.0016

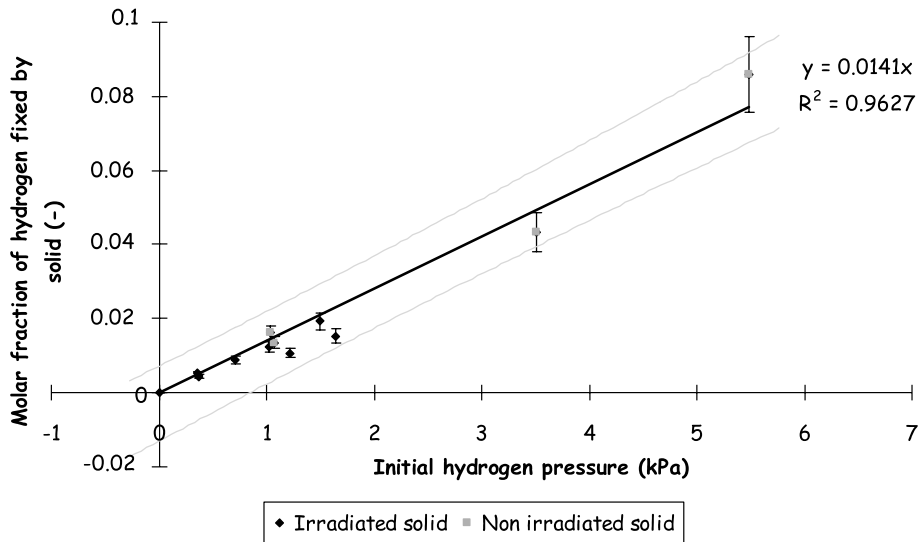


Fig. 5. Amount of hydrogen fixed by cobalt hydroxo-sulphide as a function of hydrogen initial partial pressure for a solid irradiated or not.

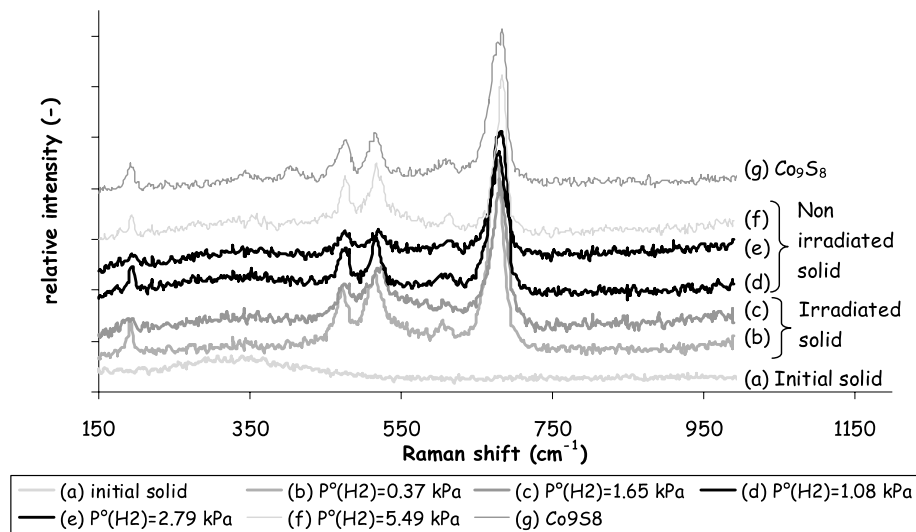


Fig. 6. Raman spectra of the initial $\text{Co}_1\text{S}_x\text{O}_y\text{H}_z$ (a) and after interaction with hydrogen at various pressures (b–f).

4. Conclusions and perspectives

To conclude, this study has shown that amorphous cobalt hydroxo-sulphide $\text{Co}_1\text{S}_x\text{O}_y\text{H}_z$ acts as a trap of hydrogen independently on propane radiolysis. Radiolytic hydrogen is rapidly produced by propane irradiation whereas the trapping of hydrogen by cobalt hydroxo-sulphide is a slower phenomenon.

In order to prove that the presence of gaseous hydrocarbons does not modify the hydrogen con-

sumption by the solid, experiments under pure hydrogen will be carried out. These experiments will also allow the determination of the maximum capacity of hydrogen storage. Recent work led to the value of 0.5 mole of H_2 per mole of Co [5].

Recent results have shown that the formation of the Co_9S_8 phase is due to a chemical reaction between hydrogen and the cobalt hydroxo-sulphide. This reaction leads to a production of H_2O and H_2S , and the kinetics of the reaction increase with temperature. It would be interesting to study the

kinetics of the phenomenon in order to propose a model which could explain and describe interaction between hydrogen and cobalt hydroxo-sulphide.

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