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Trapping of radiolytic hydrogen by amorphous cobalt oxysulfide

C. Loussot [a], C. Pichon [b,c], P. Afanasiev [a,*], M. Vrinat [a], M. Pijolat [b], F. Valdivieso [b], A. Chevarier [c], N. Millard-Pinard [c], P.C. Leverd [d]

[a] *Institut de Recherches sur la Catalyse, CNRS UPR 5401, 2 Av. A. Einstein, 69626 Villeurbanne, France*
[b] *Ecole Nationale Supérieure des Mines de Saint-Etienne, LPMG, CNRS UMR 5148, Centre SPIN, 158 cours Fauriel, 42023 Saint-Etienne, France*
[c] *Institut de Physique Nucléaire de Lyon, 4 rue E. Fermi, 69622 Villeurbanne, France*
[d] *Institut de Radioprotection et de Sûreté Nucléaire, BP. 17, 92262 Fontenay aux Roses, France*

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Abstract

Hydrogen production from the radiolysis of liquid and gaseous hydrocarbons was studied in the presence of several transition metal sulfides. Cobalt oxysulfide obtained by aqueous precipitation was the most efficient admixture to decrease radiolytic production of hydrogen by pure hydrocarbons or mixtures of saturated and unsaturated hydrocarbons. Cobalt oxysulfide was characterized by XRD, scanning and transmission microscopy, and IR spectroscopy. It seems to be amorphous compound with the impurities of lamellar $Co(OH)_2$ phase. The organic phases were analysed before and after irradiation by γ-rays or protons in order to elucidate the origin of the effect. It has been shown that the solid does not change the composition neither the amount of the organic radiolysis products, neither in liquid nor in gas phase experiments. Therefore the presence of solid does not influence any radiolysis processes in the organics. Amorphous cobalt oxysulfide acts essentially as a trap of hydrogen, being able to absorb considerable amounts of H_2 (up to 0.5 mol H_2/at. Co). The study of the solid–gas interaction showed that slow reaction of cobalt oxysulfide with hydrogen occurs at ambient conditions independently of the irradiation of the system.

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1. Introduction

Release of hydrogen from irradiated organic matter is a potential source of serious safety problems in the nuclear industry, particularly in the installations used for waste management [1–3]. A possible solution to these hazards is to diminish the production of radiolytic hydrogen by use of radical traps [4,5], energy scavengers [6,7] or hydrogen absorbers. Inorganic sulfides such as MoS_2 or RuS_2 are known to be active catalysts of hydrogen activation and of many reactions including hydrogen transfer [8–11]. At the same time some transition metals sulfides (MoS_2, RuS_2, WS_2) are known to absorb reversibly significant amounts of hydrogen [12–14]. Therefore inorganic sulfides might be of interest as inhibitors of hydrogen release. In the present work, we studied the effect of several transition metal sulfides on the radiolysis of organic solutions and gases, in order to follow their possible

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[*] Corresponding author. Tel.: +33 4 72 44 54 71.
E-mail address: afanas@catalyse.cnrs.fr (P. Afanasiev).

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effect on the release of radiolytic hydrogen and to clarify the mechanism at stake.

2. Experimental

2.1. Materials and products

In this study the alkanes used were dodecane and propane. In some experiments, mixtures of alkanes with unsaturated hydrocarbons were used such as mixtures of dodecane with methylnaphthalene (95:5) or propane with butene (50:50). Such compositions were chosen to provide easiness of detection of the hydrogenation products (if any). The organics used in the irradiation experiments included high purity grade hydrocarbons and their mixtures. Liquid alkanes and unsaturated hydrocarbons were purchased from Aldrich. Gaseous alkanes and alkenes were Messer research grade (purity = 99.95%).

The reference inorganic solids were obtained according to the methods described in earlier works: MoS_2 with 200 m^2/g specific surface area (S_{sp}) [15], RuS_2 with S_{sp} 90 m^2/g [16], CoS_2 and CoS with S_{sp} about 30 m^2/g [17]. Cobalt oxysulfide was obtained at room temperature by precipitation of aqueous cobalt nitrate (0.1 M) with aqueous $Na_2S \cdot 9H_2O$ (0.1 M). A black precipitate was immediately formed upon mixing of the reactants. The solid was filtered, washed five times with large amounts of distilled water, and dried in inert atmosphere (N_2). Since the dried solid is unstable in air and even pyrophoric when fresh (inflammation risk!), it should be stored and handled under nitrogen atmosphere.

2.2. Irradiation experiments

The irradiation experiments were conducted at ambient temperature using either γ-irradiation by ^{60}Co (1.17 and 1.33 MeV energies) or accelerated protons beam at 3.0 MeV energy (Van de Graaff 4 MV, Institut de Physique Nucléaire de Lyon). The choice of gases irradiated with proton beam is explained by the fact that the proton linear energy transfer (LET) is lower in gases than it is in liquids or solids. The proton range will thus be more important in gas. Because of its strong penetration and relatively weak interaction, the γ radiation is well adapted for the homogeneous irradiation of liquids and solids, while protons, which lose their energy quickly, are better suited for the irradiation of gases and allows to deliver comparable doses.

When using liquid organics, the irradiation was carried out in 200 ml volume stainless steel reactors equipped with manometers. The mixtures containing the liquid organics (20 ml) and weighted amount of the inorganic sulfide powder (0.2–1.6 g) were loaded under inert atmosphere (argon). Unless otherwise stated, the amount of solid was 0.8 g, for a ‘standard’ type of experiment. Argon pressure in the range 2–3 bar was applied to the reactors and they were closed by tightening the copper joints. The mixtures were irradiated by γ-rays provided by a ^{60}Co source at dose rates in the range 1.6–10 kGy/h, the total irradiation doses being in the range 0.3–4 MGy.

After irradiation, the composition of the gaseous phase in the reactors was first analysed chromatographically to determine the amount of hydrogen and light organics. Then the reactors were opened, the liquid phase and the solid were separated and analysed separately. Radiolytic hydrogen production was calculated from the total pressure and the percentage of hydrogen determined using a thermal conductivity detector.

For the irradiation of gaseous hydrocarbons, we used the specific extracted beam line associated to a gas irradiation cell set up on the 4 MV facility. The characteristics of this extracted beam line, irradiation conditions and analysis of irradiated gases are described in detail in a previous work [18]. The mixtures were irradiated at a dose rate of 50 MGy/h, the total irradiation doses applied being in the range 0.6–3.6 MGy. Hydrogen and hydrocarbons productions were analysed by gas chromatography directly coupled with the irradiation cell. Compressed cobalt oxysulfide tablets of 150 mg were placed at the bottom of the irradiation cell. The gas pressure was varied in order to modify the proton mean path length leading to the irradiation either of the gaseous hydrocarbons and the solid at the same time (for pressures of about 350 hPa) or of the hydrocarbons only (for the pressures higher than 400 hPa). These experimental conditions were designed to enable the observation of a possible effect of the irradiation of the oxysulfide.

2.3. Characterizations of the solids

The X-ray diffraction patterns were obtained on a Bruker D5005 diffractometer with CuKα emission. The diffractograms were analysed using the standard JCPDS files. Chemical analyses were performed using the atomic emission method on an AES-ICP SPECTROFLAME-ICP, model D spectrometer. Prior to analysis, the solids were dissolved in HF acid.

Scanning electron microscopy images were obtained on a Hitachi S800 device at the CMEABG centre at the Claude Bernard University in Lyon; the accelerating voltage was 25 kV. The solids were covered with Pd–Au alloy prior to measurement in order to avoid charging with electron beam. 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. Samples were mounted on a microgrid carbon polymer supported on a copper grid by placing a few droplets of a suspension of the ground sample in ethanol on the grid, followed by drying at ambient conditions. An energy dispersive analysis system (Link Isis) was used with a diode allowing detection of the light elements ($Z > 5$).

The gaseous products evolved upon heating of the solids were studied using a mass-spectrometer Gas Trace A (Fison Instruments) equipped with a quadrupole analyser working in a Faraday mode. The solids (ca. 0.5 g) were heated from room temperature to 1000 °C in a quartz cell at the heating rate of 5 K min^{-1}. A silica capillary tube heated at 180 °C continuously bled off a proportion of the gaseous reaction products.

3. Results and discussion

3.1. Synthesis and characterization of amorphous cobalt oxysulfide

Cobalt oxysulfide, which appeared to be the most important solid for this work, is not a well characterized compound. According to Jelinek [19], the primary precipitates from Co(II) and basic sulfide solutions, the precipitates of composition $Co(OH,SH)_2$ are formed, with the OH^- content depending on pH. The chemical nature of such precipitates is disputable. It seems to be highly unstable in aerobic conditions. Dönges [20,21] supposed that Co(III) basic CoSOH sulfide is formed, whereas de Medicis [22] suggested that the solid disproportionate oxidatively to $Co(OH)_2$ and CoS_2 mixtures. However no solid evidence was provided for any of these hypotheses.

Powder X-ray diffraction (Fig. 1) shows that the product synthesized was mainly amorphous, but contained some cobalt hydroxide impurity. This $Co(OH)_2$ might be formed due to the hydrolysis of sulfide ions in the aqueous solutions

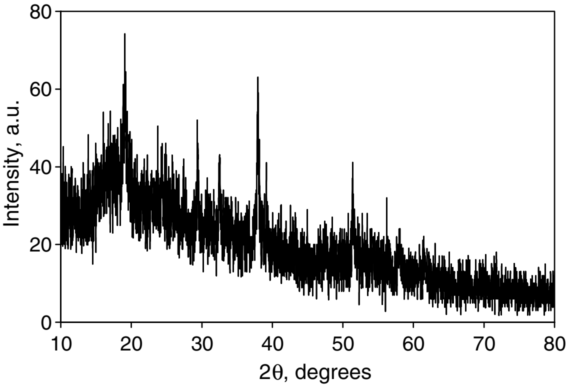

Fig. 1. XRD pattern of the cobalt oxysulfide after drying. All peaks correspond to the $Co(OH)_2$ impurity phase. Note that the noise level is comparable to the peak intensity.

$$S^{2-} + H_2O = SH^- + OH^- \qquad (1)$$

Since for the reaction (1) the equilibrium is completely shifted to the right side in a large pH range [23], considerable amounts of hydroxide are present in the Na_2S solutions. Due to the basic pH of the solution, hydroxide precipitation seems to be possible as a side process.

Transmission electron microscopy reveals a high degree of dispersion of the amorphous matter and confirms the existence of rare inclusions of lamellar $Co(OH)_2$ phase (Fig. 2), corresponding to several per cent of the solid volume. Energy dispersed X-ray analysis, in a scanning electron microscope, within the amorphous matter gave a Co:S atomic ratio close to 1 and showed the good homogeneity of the sample (Fig. 3).

The analysis of the infrared spectrum shown in Fig. 4 indicated the presence of water (large band between 3000 and 3600 cm^{-1} due to $\nu(HO–H \cdots H)$ mode and band at 1645 cm^{-1} due to $\delta(HOH)$ in water). The presence of bands at 3630 cm^{-1} (due to $\nu(HO)$ mode), 1090 and 620 cm^{-1} (due to $\nu(S–O)$ modes), revealed the presence of hydroxide and sulfate groups respectively [24].

Complete chemical analysis (CNRS Solaize) gives the following weight fractions of the composing elements: 43.9% Co, 27.7% S, 24.8% O and 1.4% H on average. Elemental compositions of samples of $CoS_xH_yO_z$ from different preparations are presented in Table 1, demonstrating variability of its composition. However, limiting the values of x,

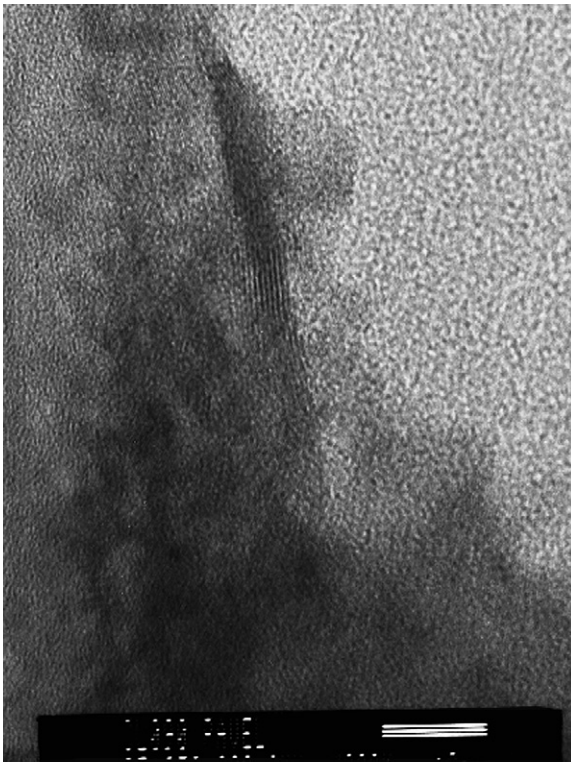

Fig. 2. Transmission microscopy image of cobalt oxysulfide representing an inclusion of a lamellar $Co(OH)_2$ crystallite in the amorphous matrix of $CoS_xH_yO_z$.

y and z seem to be are not far from the stoichiometric formula CoS(OH).

As follows from the characterizations, the solid is amorphous, without indications on any strong disproportionation, since only very low content of $Co(OH)_2$ was observed in dry precipitates and CoS_2 phase was not evidenced. Chemical analysis corroborates earlier results of Dönges and de Medicis [20–22].

3.2. Possible effects of solids on the radiolysis of organic compounds

The studies of hydrocarbons radiolysis have revealed a rich chemistry involving the initial ionic species produced [25]. Radiolysis of hydrocarbons occurs through formation of radical cations and their disappearance via ion-molecule reactions. Although the hydrocarbon radiolysis is one of the most comprehensively studied (beside probably that of liquid water), a lot of understanding problems persist, caused by insufficient knowledge of short-lived intermediates and the complexity of spur dynamics. Detailed radiolysis mechanisms which are still disputable, can be found elsewhere [26,27]. Due to complexity of the radiolysis phenomena, we do not even try here to provide any new insight on them, or to analyse radiolysis yields, but only observe the influence of the solid on the products composition in order to make some qualitative conclusions.

The composition of the radiolysis products and the radiolytic H_2 yield might be influenced in different ways by the presence of solids. Radiolytic yield of hydrogen might be increased, decreased or remain unaffected due to the presence of some solids in the irradiation zone [28,29]. If a solid decreases the apparent radiolytic production of hydrogen by a liquid or a gas, then three fundamentally different assumptions about the nature of this effect might be proposed, all leading to different and experimentally distinguishable consequences:

1. In a mixture of saturated and unsaturated hydrocarbons, the solid might induce catalytic hydrogenation of the unsaturated hydrocarbons by the H_2 released from the radiolysis. In this case, the composition of the organic reaction products

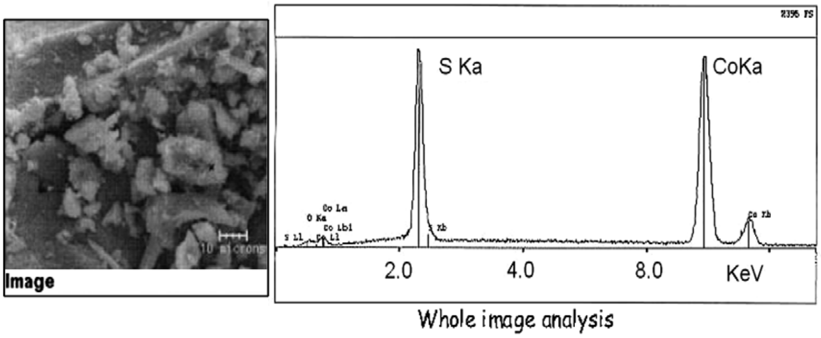

Fig. 3. Scanning microscopy image representing morphology of the $CoS_xH_yO_z$ solid and energy dispersed X-ray analysis.

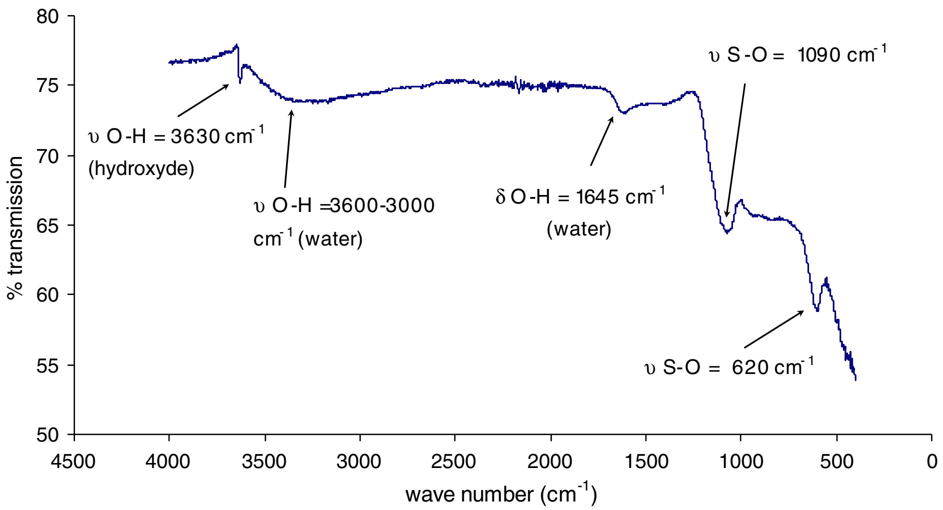

Fig. 4. Infrared spectrum of the $CoS_xH_yO_z$ specimen.

Table 1
Compositions of samples from different preparations after precipitation, washing and drying

Solid number	Chemical formula
1	$CoS_{1.11}H_{0.78}O_{1.00}$
2	$CoS_{1.38}H_{1.14}O_{1.61}$
3	$CoS_{1.18}H_{0.73}O_{1.28}$
4	$CoS_{1.13}H_{1.20}O_{1.50}$
5	$CoS_{1.17}H_{2.37}O_{2.15}$
6	$CoS_{1.08}H_{1.43}O_{1.72}$
7	$CoS_{1.03}H_{1.07}O_{1.54}$
8	$CoS_{1.16}H_{1.41}O_{2.24}$
9	$CoS_{1.10}H_{0.95}O_{1.53}$
10	$CoS_{1.25}H_{2.66}O_{2.79}$
11	$CoS_{1.22}H_{1.94}O_{2.53}$

should be significantly changed when radiolysis occurs in the presence of the solid. Hydrogenation products should be formed and the effect of the solid should be time-limited, until all unsaturated hydrocarbons available are hydrogenated or until all the available hydrogen is consumed. Irradiation might also affect the catalytic properties of the irradiated solid [30,31].

2. The solid might act as an energy scavenger or as a radical trap, participating in the energy dissipation by the non-thermalised species. In this case, the amount of both radiolytic hydrogen and of organic radiolysis products should be changed in step. The effect of the solid should be observed whatever the radiation dose, or at least in a very wide range of doses.
3. The solid might absorb hydrogen by means of dissolution and/or chemical reaction. In this case, the composition of the organic phase should not be drastically changed. The effect of the solid should be limited by its capacity to absorb hydrogen.

In the present work, we considered all three possibilities and verified whether the results of our experiments were compatible with any of them. Two model mixtures of hydrocarbons were chosen, providing the possibility to check the effects of the solid presence both in the liquid and gaseous phase. Moreover, the radiation chemistry of butane is different than that of propane since gas radiolysis mechanisms are different than those in liquid. Then, methylnaphnatele is a triplet excited state scavenger and butene is a radical scavenger. Therefore the complementary information can be provided from the analysis of the differences in the radiolysis products (but there are no any, vide infra).

3.3. Irradiation of mixtures methylnaphthalene–dodecane and propane–butene in the presence of metal sulfides

To verify if a catalytic reaction was taking place during irradiation, the γ-radiolysis of mixtures of methylnaphthalene and dodecane (5–95 vol.%) was performed in the presence of various inorganic sulfides and compared to that of the same mixtures without addition of the sulfides. Solids with well-known catalytic functionality were used, like highly dispersed MoS_2 and RuS_2. Amorphous and crystalline cobalt sulfides were tested as well. As can be seen from Fig. 5, which presents the amount of hydrogen in the gas phase after an irradiation dose of 2 MGy, the production of radiolytic hydrogen is somewhat decreased due to the presence of all solids. However the most pronounced effect is observed for the amorphous cobalt oxysulfide, which is not known to be a good hydrogenation catalyst.

The quantitative analysis of the gaseous radiolysis products by GC and mass spectrometry showed that H_2 was the main product representing more than 95%, the rest being volatile hydrocarbons such as CH_4, C_2H_6, C_2H_4 and C_3H_8. As revealed by the analysis of the other organic radiolysis products, they essentially include scission and cross-linking products. Hydrogenated methylnaphtalenes were never encountered in the liquid products.

The same conclusion can be inferred from the experiments with gaseous hydrocarbons. Fig. 6 shows the irradiation products produced by a 3 MeV protons beam on a propane–butene mixture in the presence or in the absence of $CoS_xH_yO_z$ at a dose of 0.6 MGy. The two mains peaks correspond to the unreacted propane and butene. At retention times lower than the one of propane, several peaks were observed due to C_1–C_2 *n*-alkanes and alkenes. Between C_3 and C_4 peaks, isopropane is observed. Above the butene peak, branched C_4–C_8 hydrocarbons are detected. In agreement with the results on γ-irradiation of dodecane, the amounts of produced hydrocarbons remained unchanged whatever the duration of contact between the irradiated gas and the oxysulfide was, whereas the amount of radiolytic hydrogen decreased gradually during this same duration.

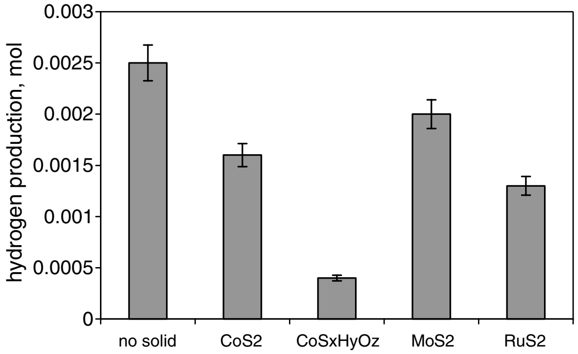

Fig. 5. Hydrogen production in the dodecane (95 vol.%)–methylnaphthalene (5 vol.%) mixture after irradiation at 2 MGy dose in the presence of several dispersed metal sulfides (the amount of solid in all experiments was 0.8 g, dispersed in 200 ml of liquid hydrocarbons mixture).

It follows from the above experimental results, that the hypothesis about catalytic re-hydrogenation of unsaturated compounds can be eliminated.

3.4. Irradiation of dodecane and propane in the presence of cobalt oxysulfide

Radiolysis of pure alkanes and particularly that of dodecane and propane allows easier analysis of the radiolysis products and at the same time eliminates all the complex reciprocal effects in radiolysis between hydrocarbons and aromatic compounds, known to be very significant [26]. As the most efficient hydrogen release inhibitor was cobalt amorphous oxysulfide, we focused our study on this solid and some related compounds, such as cobalt sulfide, hydroxide and sulfate.

The amounts of hydrogen released at different doses by pure dodecane and by its mixtures with amorphous cobalt sulfide as well as crystalline cobalt sulfide, hydroxide and sulfate of sodium nitrate (possible impurity in the precipitation brines) are represented in Fig. 7. It follows from the results that only the oxysulfide $CoS_xH_yO_z$ solid strongly decreases the radiolytic production of hydrogen gas, whereas other solids are absolutely inefficient. For the highest irradiation doses and in the presence of $CoS_xH_yO_z$, weak but non-negligible amounts of hydrogen sulfide were detected in the gaseous radiolysis products, its content being measured by hundreds of ppm (about 300 ppm for the dose of 2 MGy as measured by HNU H_2S-sensible photodetector).

The results of GC and mass spectrometry analysis of the condensed phase show the presence of scission and cross-linking products. In Fig. 8 the products of irradiation of pure *n*-C_{12} and its mixture with $CoS_xH_yO_z$ are shown. The main peak is due to the unreacted *n*-C_{12}. At lower retention time values, several peaks were observed due to C_5–C_{11} *n*-alkanes and alkenes (scission products). After the C_{12} peak, cross-linking compounds were detected, which are all branched C_{21}–C_{24} paraffins. The most important finding of the organic phase analysis is the striking similarity between the chromatograms in Fig. 8. Indeed, detailed consideration of heavier products shows nearly perfect coincidence of all peaks positions and intensities. This means that neither the composition nor the

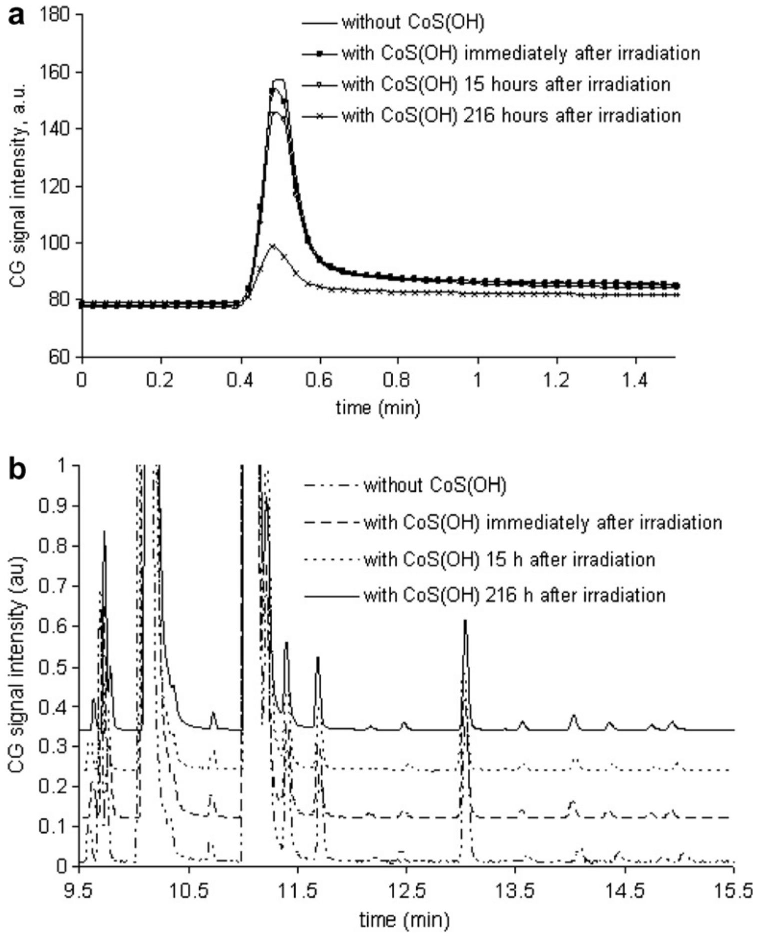

Fig. 6. Chromatograms of the reaction products of the propane–butene (50–50 vol.%) mixture irradiated in the absence and in the presence of $CoS_xH_yO_z$ solid, (a) representing hydrogen signals and (b) hydrocarbons signals.

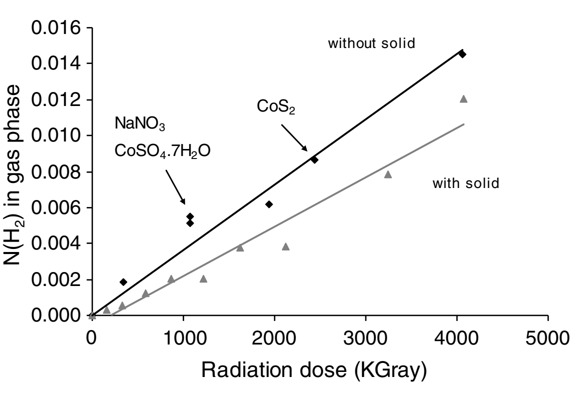

Fig. 7. Radiolytic hydrogen production by dodecane and its mixtures with several cobalt containing inorganic compounds as a function of the irradiation dose.

amount of the organics produced was affected by the presence of cobalt oxysulfide, whereas the amount of hydrogen was decreased by a factor of three. Similarly, in the case of propane irradiation by protons, the experiments performed with or without cobalt oxysulfide showed exactly the same composition of hydrocarbons. This excludes the hypothesis of solid action through an energy scavenging mechanism.

Since during the γ-irradiation, the dose rate was low, the speed of hydrogen production was also low (days and weeks to obtain considerable amounts of hydrogen). On the contrary, in the case of protons irradiation, the mixtures of hydrocarbons and oxysulfide were irradiated at (higher dose rates with the) total doses varying between 0.6 and 3.6 MGy. The mixture was irradiated during 45 min to obtain a total dose of 0.6 MGy with the corresponding release of hydrogen. Immediately after irradiation, no hydrogen absorption was observed, whereas 15 h after the irradiation, a slight decrease (6%) of the amount of hydrogen in the gas

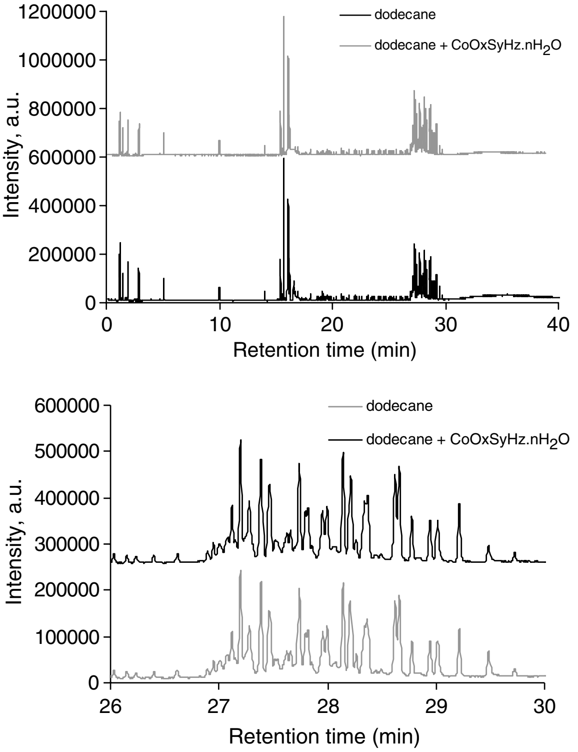

Fig. 8. Chromatogram of the radiolysis products at 2 MGy dose: dodecane alone (bottom) and dodecane in the presence of the $CoS_xH_yO_z$ solid (top).

phase could be measured, which is even more important after 216 h of contact (70%). Therefore, in the presence of cobalt oxysulfide, the amount of hydrogen in contact with the solid decreases slowly versus time once the protons irradiation has been stopped, suggesting that the solid has the ability to absorb this gas.

Summarizing the above presented results, it can be concluded that only H_2 trapping by the solid occurs, independently of the radiolysis of organics. Moreover, the fact that no difference of hydrogen storage between γ and protons irradiations could be observed is another argument in favour of hydrogen sorption.

To check the direct solid–gas reaction, we put the cobalt oxysulfide in contact with pure hydrogen. Thus, a tablet of 150 mg of oxysulfide was introduced in a 20 ml volume stainless steel cell equipped with a piezoelectric pressure gauge, which is insensitive to the nature of gas and allowed us to follow the variation of pressure versus time. Before introducing hydrogen, the cell was evacuated with a primary pumping (less than 10^{-2} hPa). Then, 100 hPa of hydrogen were added into the cell. This pressure was chosen to be under the same conditions as in the irradiation experiments. Fig. 9 shows the hydrogen pressure variation as a function of time. The hydrogen pressure decreases slowly up to an asymptotic limit value of about 20 hPa. This pressure variation corresponds to hydrogen storage of 0.5 mol/mol. In the case of protons irradiation of propane, for the same conditions of hydrogen partial pressure and oxysulfide weight, we obtained a hydrogen consumption of 0.4 mol/mol. So, we can conclude that:

- Cobalt oxysulfide absorbs molecular hydrogen at ambient conditions.
- The amount of hydrogen absorbed by the oxysulfide is the same with and without irradiation.

Cobalt oxysulfide prepared in this study had specific surface area in the range 50–70 m^2/g depending on the preparation batch. As appears from the qualitative estimation, the hydrogen amount which can potentially be adopted by the surface of the solids tested is small (1–5% order of magnitude), compared to the observed effects of trapping Therefore the surface area does not play primary role to determine the quantity of hydrogen absorbed. However it might of course affect the process kinetics, which is not considered in this work, dealing mostly with long time effects.

Further, we have tried higher pressures for hydrogen storage (between 100 hPa and 0.4 MPa). It was observed that above about 0.13 MPa, hydrogen storage capacity is quite constant to 0.5 mol of hydrogen per mole of initial solid. Our preliminary studies show that the trapping of hydrogen is irreversible. The chemical mechanism of trapping seems to be complex and will be published

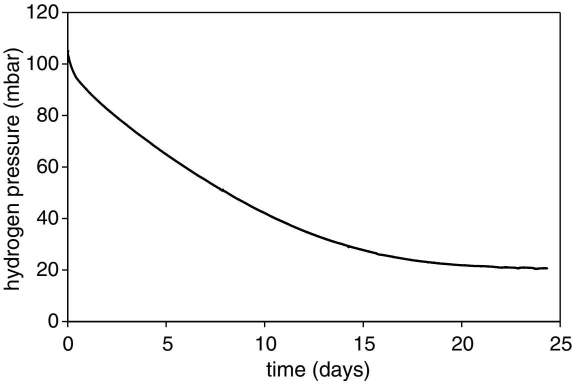

Fig. 9. Hydrogen absorption by the $CoS_xH_yO_z$ solid: hydrogen pressure evolution in the cell as a function of time.

elsewhere. To better understand the mechanism of hydrogen trapping further work is necessary. We will study the hydrogen absorption by cobalt oxysulfide and characterize in detail the solids before and after hydrogen absorption.

4. Conclusion

The goal of this work was to give an insight on the decrease of radiolytic production of hydrogen by hydrocarbons induced by inorganic sulfides and particularly by that of cobalt. On the whole, the experimental data indicate that considerable amounts of hydrogen can be trapped within the amorphous cobalt oxysulfide at ambient temperature, in a wide range of pressures, at least from 10 to 500 hPa. The maximum amounts of trapped hydrogen are estimated. This result is in agreement with recent patent literature where amorphous sulfides are suggested as hydrogen getters [32]. The amount of trapped hydrogen appears to depend on the precipitate composition and treatment. For the amorphous sulfide $CoS_xH_yO_z$ with a stoichiometry close to the CoS(OH) formula nearly 0.5 mol of hydrogen per mole of initial solid can be absorbed within the solid. This seems to be a purely chemical or physical phenomenon, the effects of radiation on the solid–gas interaction being negligible.

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