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Dedicated to the memory of Professor
I.G. Murgulescu (1902–1991)

USE OF SOME CATALYSTS IN RADIOLYTICAL SPLIT OF WATER

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The present paper deals with the study of catalyzed water radiolysis under the influence of γ-rays emitted by a ^{60}Co source ($\Lambda = 3 \times 10^4$ Ci) with a dose rate of 8.3 kGy/h, for hydrogen production. Thirty-one solid inorganic compounds, insoluble in water, were tested as catalysts. They belong to: coordination compounds of some metallic ions with organic ligands based on salycilaldehyde or naphthalenaldehyde derivatives, mixed oxides, $RhCl_3$ supported on a Al_2O_3 layer and bimetallic compounds with EDTA ligand. The released hydrogen quantity, determined by mass spectrometry, was approximately 7-35 times greater than the one produced by simple radiolysis of water, in the absence of catalysts.

INTRODUCTION

The water radiolysis for hydrogen output under different experimental conditions by the action of ionizing nuclear radiations or the neutrons inside of a nuclear reactor was studied exhaustively by several authors.[1-5]

The present paper continues a previous research concerning the hydrogen production by catalyzed water radiolysis, under the influence of γ-rays, emitted by a ^{60}Co radioactive source with the activity of 3×10^4 Ci and a dose rate of 8.3 KGy/h, at a 0.3 m irradiation distance.

Various inorganic compounds, which resisted the action of nuclear radiations and were water insoluble, were tested as catalysts. The radiolysis products are identified and measured by mass spectrometry. The ^{60}Co irradiation source simulated the nuclear radiations emitted by the fission products as high-level activity radioactive wastes, which could by used for such applied research.

EXPERIMENTAL

Samples preparation

Some vials of 30 mL capacity, filled with a certain catalyst quantity and 10 mL of distilled water, were employed. These vials were hermetically closed with rubber corks, covered at exterior with paraffin, in order to keep inside the radiolysis products appeared due to irradiation. A blank sample, without catalyst, for comparison purposes, was also prepared.

The hermetically closing was verified by producing hydrogen from the following chemical reaction:

$$Zn + 2HCl \rightarrow ZnCl_2 + H_2 \uparrow \tag{1}$$

in a vial, immersed into a water tank. No hydrogen release was noticed as gas bubbles even after one week.

Irradiation

The irradiation was realized employing a ^{60}Co source ($\Lambda = 3 \times 10^4$ Ci) which simulated the high activity radioactive wastes that could be used in such experiments in order to obtain radiolytically hydrogen in the presence of catalysts.

The prepared samples were irradiated by γ-rays emitted by the ^{60}Co source for 24 h, at a dose rate of 8.3 KGy/h and at a radial distance $\phi = 0.3$ m. The whole experimental device was immersed into a water basin.

The radiolysis products

In order to identify the radiolytic products together with other chemical species such as H_2, O, $HO^{\bullet}$, O_2, H_2O_2, etc., including the nitrogen and oxygen from the air above the 10 mL of water as irradiated sample, a special method based on mass spectrometry was used.

A chromatographic needle was fixed at the entrance of the mass spectrometer, but with its sharp end it can penetrate the rubber cork of the irradiated sample under analysis. Before working with a new sample, the mass spectrometer was emptied of the gaseous products from the previous sample, realizing a 10^{-7} Torr vacuum.

The obtained results were recorded using a PC and printed in separate tables, as mass number *vs.* peak intensity.

In order to calibrate the mass spectrometer which means the transformation of the peak intensity (given in arbitrary units) corresponding to the species with the mass number 2 into the real hydrogen amount, in grams, the above mentioned chemical reaction was repeated. Therefore, 0.1 g of Zn powder put into 0.1 n HCl leads to a hydrogen quantity of 3.12×10^{-3} g, which corresponds to a 7.66×10^5 a.u. peak intensity.

Radiochemical yield of hydrogen output

Taking into account the equivalence between the peak intensity in mass spectrograms for the species with mass number 2 and the real amount of hydrogen resulting from the above mentioned calibration reaction, radiochemical yield (G_{H_2}) can be established as follows:

– 3.12×10^{-3} g H_2 in 10 mL solution correspond to 0.15 mole H_2 / kg solution

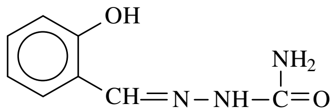
– Absorbed dose for 24 h irradiation time is: 8.3 kGy/h × 24 h = 1.99×10^5 J/kg

– $$G_{H_2} = \frac{0.15 \times 6.023 \times 10^{23}}{1.99 \times 10^{5} \times 6.24 \times 10^{16}} = \frac{7.27\text{molecules}}{100\text{eV}}$$ (where 1J = 6.24×10^{18} eV).

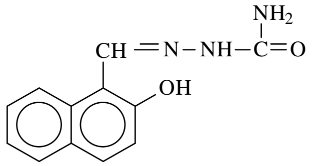
The complex compound with Cu^{2+}, La^{3+}, Ni^{2+}, Pb^{2+}, Gd^{3+} and Ba^{2+} ions with some organic ligands were provided by quoted authors.[6-8] The ligands are presented in the note. As organic ligands, some derivates resulted after condensation reactions between salicylaldehyde or naphthalenaldehyde and hydroxylamine or hydrazine, under several experimental conditions, were employed. Fluka Co. offered the other solid compounds.

Note

L_1 =

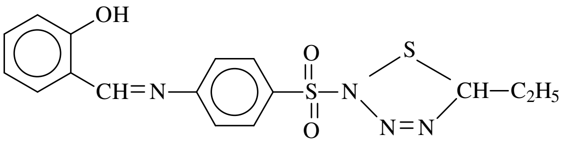


L_2 =

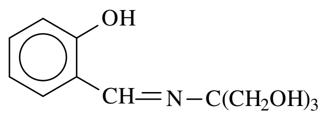


$L_3 = H_2N—C(CH_2OH)_3$

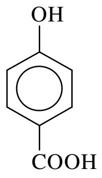
L_4 =



L_5 =



L_6 =



The crystalline structures of all these compounds were determined by X-rays diffractograms, noticing that they remained unchanged after irradiation. This is a proof of their catalyst role for the hydrogen output by water radiolysis.

RESULTS AND DISCUSSION

The water radiolysis process could be drawn as follows:[9-11]

$$\rightsquigarrow H_2O \longrightarrow H_2O^* \longrightarrow H^\bullet + HO^\bullet \tag{2}$$

$$\rightsquigarrow H_2O \longrightarrow H_2O^+ + e^- \tag{3}$$

$$H_2O + e^- \longrightarrow H_2O^- \tag{4}$$

$$H_2O^+ + H_2O^- \longrightarrow 2\,H_2O^* \longrightarrow 2\,H^\bullet + 2\,HO^\bullet \tag{5}$$

$$H^\bullet + H^\bullet \longrightarrow H_2 \tag{6}$$

$$HO^\bullet + HO^\bullet \longrightarrow H_2O + O \tag{7}$$

$$HO^\bullet + HO^\bullet \longrightarrow HO_2^\bullet + H^\bullet \tag{8}$$

$$H^\bullet + O \longrightarrow HO^\bullet \tag{9}$$

In the catalyst presence, the first stage could be an excited state under the influence of γ-radiations, which permits the attachment of an excited water molecule on its surface:[12]

$$\rightsquigarrow X \longrightarrow X^* \text{ (activated state)} \tag{10}$$

$$\rightsquigarrow H_2O \longrightarrow H_2O\ ^* \text{ (activated state)} \tag{11}$$

$$X^* + H_2O^* \longrightarrow [H_2O{\cdot}X]\ ^{**} \text{ (activated compound on the surface)} \tag{12}$$

$$[H_2O{\cdot}X]\ ^{**} \longrightarrow H\bullet + HO\bullet + X + h\nu\ \ldots \tag{13}$$

$$X = \text{catalyst}$$

In this way, the activated compound decomposes, furnishing a lot of radiolysis products, afterward identified by mass spectrometry. The obtained experimental data are summarized in Table 1.

The data of Table 1 show that, for any experiment, the total oxygen amount (m_1), as a summation of the volumes (peak intensities) of the products determined in the mass spectrograms:

$$m_1 = [O] + [HO^\bullet] + [O_2]$$

is higher than that found in the air (m_2). The last quantity could be computed taking into account the volumes of nitrogen species, from mass spectrograms:

$$m_2 = 0.23\cdot([N]+[N_2])$$

Table 1

Peak intensity values (arbitrary units) of principal species founds in mass spectrograms after 24 h irradiation time in several experiments on catalyzed radiolysis of water

No.	Catalyst	Amount (g)	Peak intensity (a.u.) for:							G_{H_2}
			H_2 (2)	O (16)	$HO^\bullet$ (17)	O_2 (32)	H_2O (18)	N (14)	N_2 (28)	
1.	$Cu(L_1\text{-}H)NO_3$	0,1	937270	40100	148290	60960	518550	48790	628990	3.81
2.	$Cu(L_2\text{-}H)Cl$	0,1	927680	35830	149950	46010	526940	39150	660360	3.70
3.	$La(L_3\text{-}H)_3$	0,1	888570	41260	153090	123570	534310	57860	981810	3.52
4.	$Ni(L_4\text{-}H)_2$	0,1	1163250	43790	246110	141620	635310	64490	859310	4.64

No.	Catalyst	Amount (g)	Peak intensity (a.u.) for:							G_{H_2}
			H_2 (2)	O (16)	$HO^\bullet$ (17)	O_2 (32)	H_2O (18)	N (14)	N_2 (28)	
5.	$Pb(L_5\text{-}H)_2$	0,1	1131630	48650	191390	85600	656990	35650	586680	4.53
6.	$Gd(L_1\text{-}H)_3$	0,1	728940	40920	185220	52930	640930	33710	546820	2.91
7.	$Ba(L_6\text{-}H)_2$	0,1	1293040	43620	179710	100100	629040	48910	971590	5.16
8	$La(L_1\text{-}H)_2$	0,1	1375100	64420	220860	224730	804200	74574	1440200	5.48
9.	Cu(Bi EDTA)$_2$	0,1	1636860	47460	146620	39060	519060	37900	641410	6.52
10.	Pb(Bi EDTA)$_2$	0,1	952020	44460	197800	68510	687260	29300	476530	3.80
11.	1,2[$Co(NH_3)_4(NO_2)_2$]Bi EDTA	0,1	1274380	45180	187980	65770	652470	32060	514640	5.08
12.	$La_2O_3 \cdot CuO$	0,1	646470	37810	161170	65460	564300	30810	506320	2.58
13.	$La_2O_3 \cdot Co_2O_3$	0,1	1433020	40630	151450	104970	528030	40020	719670	5.72
14.	$La_2O_3 \cdot Cr_2O_3$	0,1	959280	39020	158290	82600	548440	37550	639120	3.83
15.	$La_2O_3 \cdot Fe_2O_3$	0,1	1051310	54890	218370	157260	762950	58850	1024880	4.20
16.	$La_2O_3 \cdot Ni_2O_3$	0,1	937130	39750	160970	125620	555180	48910	825530	3.74
17.	1/2 $Co_2O_3 \cdot Bi_2O_3$	0,1	780840	44508	151110	92210	526890	41000	705630	3.12
18.	$NiO \cdot Bi_2O_3$	0,1	974750	63430	252600	170550	867270	64280	1074640	3.89
19.	$PbO \cdot Bi_2O_3$	0,1	1023620	36630	157950	50960	545800	24520	390250	4.08
20.	1/2 La_2O_3 · 3/2 Bi_2O_3	0,1	1906620	36950	147060	53690	521140	39330	652560	7.50
21.	$RhCl_3/Al_2O_3$	0,1	948010	54340	229320	92010	788610	41090	672400	3.79
22.	$RhCl_3/Al_2O_3$	0,2	1080640	42110	177960	75840	624330	38750	661400	4.32
23.	$RhCl_3/Al_2O_3$	0,3	1242350	52120	190930	65130	664070	33670	532630	4.96
24.	$RhCl_3/Al_2O_3$	0,4	2154850	34050	145800	37810	523880	30200	539230	8.60
25.	$RhCl_3/Al_2O_3$	0,5	3992560	50700	192610	92450	671060	41570	724830	15.96
26.	$Cu(L_1\text{-}H)NO_3$	0,2	1079840	62360	241390	27010	668520	65870	176460	4.29
27.	$Cu(L_1\text{-}H)NO_3$	0,3	1082010	38810	162390	59690	561350	30170	483770	4.32
28.	$Cu(L_1\text{-}H)NO_3$	0,4	1190050	68590	252260	136320	881660	64880	964520	4.75
29.	$Cu(L_2\text{-}H)Cl$	0,2	868810	55850	248860	79900	847510	41870	672450	3.47
30.	$Cu(L_2\text{-}H)Cl$	0,3	1129380	63260	255020	149530	877860	60050	986300	4.48
31.	$Cu(L_2\text{-}H)Cl$	0,4	977690	61050	237770	164730	830260	60800	1036250	3.90

The difference, $m_3 = m_1 – m_2$, corresponds to the oxygen quantity practically resulted only from the radiolysis process. On the other hand, taking into account the hydrogen amount found by mass spectrometry, one could estimate a "theoretical" oxygen quantity (m_4), which should result, from water split:

$$1 \text{ vol. } H_2O \rightarrow 1 \text{ vol. } H_2 + 0.5 \text{ vol. } O_2$$

Comparing the m_3 and m_4 values presented in Table 2, one can observe that they are not equal to each other, due to the fact that a certain part of the oxygen could be dissolved in the 10 mL of water, or could be absorbed on the catalyst surface, etc.

From the structure determinations using X-rays diffraction, one can notice that the spectra are to a certain extent identical for the respective substances, before and after irradiation, which proves their catalytic role in the radiolysis process. Some little displacements of X-rays peaks for the irradiated catalysts to the bigger 2θ values are due to a small increase of the size of the elementary cells, but not due to the phase modifications. Some of these results are presented in the Figs. 1-6.

Table 2

The agreement between theoretical and practical amounts of O_2 in the experiments connected to catalysed water radiolysis

No.	Catalyst	Amount (g)	Amount of Oxygen (arbitrary units)			
			Total (m$_1$)	From air composition (m$_2$)	Found from radiolysis only (m$_3$)	Theoretical accounted (m$_4$)
1.	$Cu(L_1\text{-}H)NO_3$	0,1	249350	155889	93460	468635
2.	$Cu(L_2\text{-}H)Cl$	0,1	231790	160887	70902	463840
3.	$La(L_3\text{-}H)_3$	0,1	317920	239124	78795	444285
4.	$Ni(L_4\text{-}H)_2$	0,1	431520	212474	219045	581625
5.	$Pb(L_5\text{-}H)_2$	0,1	325640	143135	182504	565815
6.	$Gd(L_1\text{-}H)_3$	0,1	279070	133521	145548	364320
7.	$Ba(L_6\text{-}H)_2$	0,1	323430	234715	88715	646520
8.	$La(L_1\text{-}H)_2$	0,1	510010	348398	161611	687550
9.	$Cu(Bi\ EDTA)_2$	0,1	233110	156241	76868	818430
10.	$Pb(Bi\ EDTA)_2$	0,1	310770	116340	194429	478010
11.	$1,2[Co(NH_3)_4(NO_2)_2]Bi\ EDTA$	0,1	298930	125741	173189	637190
12.	$La_2O_3 \cdot CuO$	0,1	264460	123539	140921	323235
13.	$La_2O_3 \cdot Co_2O_3$	0,1	297050	174728	122321	716510
14.	$La_2O_3 \cdot Cr_2O_3$	0,1	279910	155634	124275	479640
15.	$La_2O_3 \cdot Fe_2O_3$	0,1	290520	249257	41262	525655
16.	$La_2O_3 \cdot Ni_2O_3$	0,1	326340	201121	125218	468565
17.	$1/2\ Co_2O_3 \cdot Bi_2O_3$	0,1	287820	171724	116095	390420
18.	$NiO \cdot Bi_2O_3$	0,1	486580	261951	224628	487375
19.	$PbO \cdot Bi_2O_3$	0,1	245540	95397	150142	511810
20.	$1/2\ La_2O_3 \cdot 3/2\ Bi_2O_3$	0,1	237700	159134	78565	953310
21.	$RhCl_3/Al_2O_3$	0,1	178572	164102	14469	474005
22.	$RhCl_3/Al_2O_3$	0,2	375670	161034	214635	540320
23.	$RhCl_3/Al_2O_3$	0,3	305960	130248	175711	621175
24.	$RhCl_3/Al_2O_3$	0,4	217660	130968	86691	1077425
25.	$RhCl_3/Al_2O_3$	0,5	335760	181861	153899	1996280
26.	$Cu(L_1\text{-}H)NO_3$	0,2	330760	55735	275024	539920
27.	$Cu(L_1\text{-}H)NO_3$	0,3	260890	118206	142683	541005
28.	$Cu(L_1\text{-}H)NO_3$	0,4	457170	236762	220408	595025
29.	$Cu(L_2\text{-}H)Cl$	0,2	384610	164293	220316	484405
30.	$Cu(L_2\text{-}H)Cl$	0,3	467810	240660	227149	564690
31.	$Cu(L_2\text{-}H)Cl$	0,4	463550	252325	211228	588845

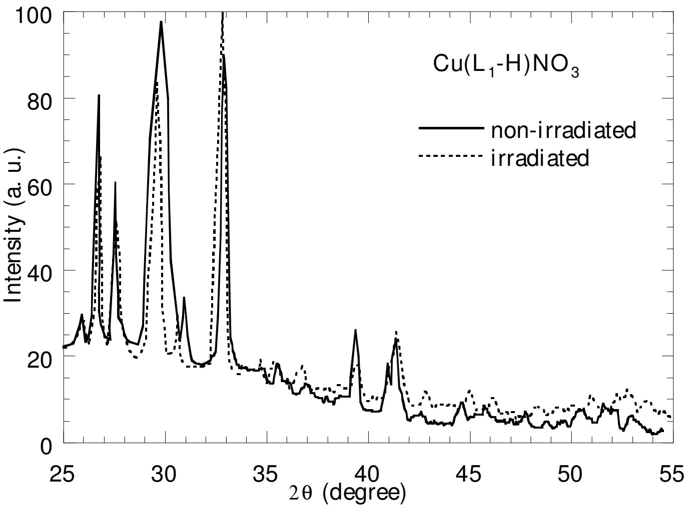


Fig. 1 – X-rays diffractograms for $Cu(L_1\text{-}H)NO_3$, before and after γ-irradiation.

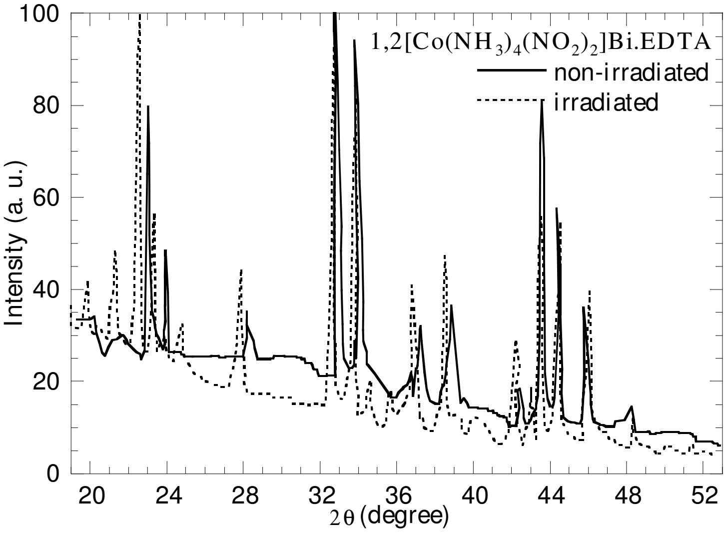


Fig. 2 – X-rays diffractograms for 1,2$[Co(NH_3)_4(NO_2)_2]$Bi EDTA, before and after γ-irradiation.

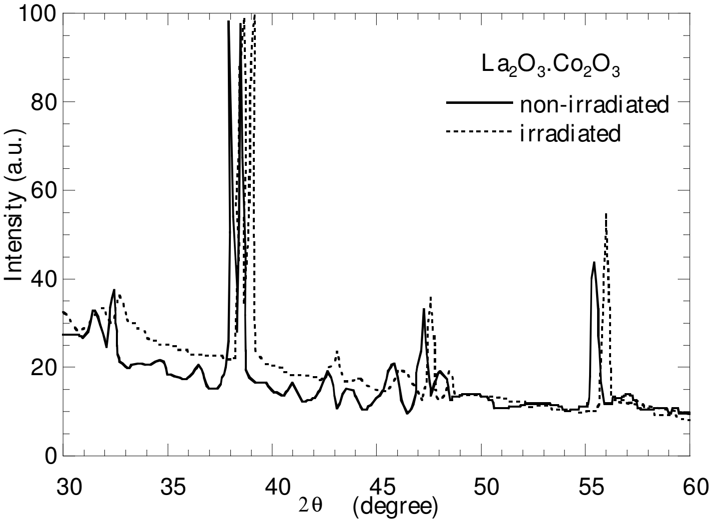


Fig. 3 – X-rays diffractograms for $La_2O_3 \cdot Co_2O_3$, before and after γ-irradiation.

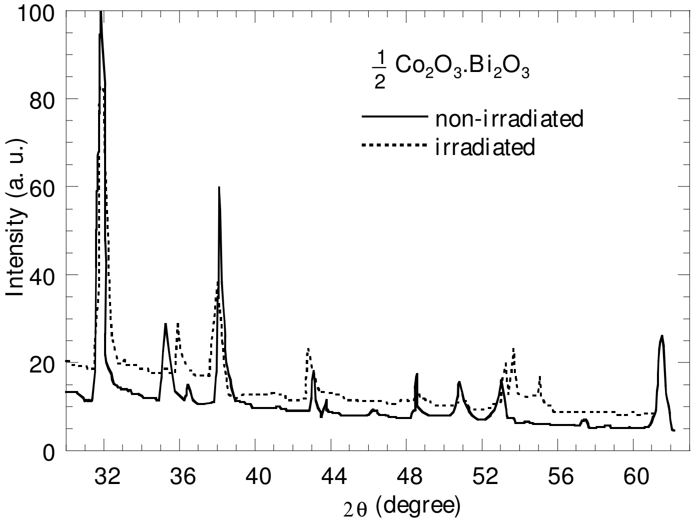


Fig. 4 – X-rays diffractograms for 1/2 $Co_2O_3 \cdot Bi_2O_3$, before and after γ-irradiation.

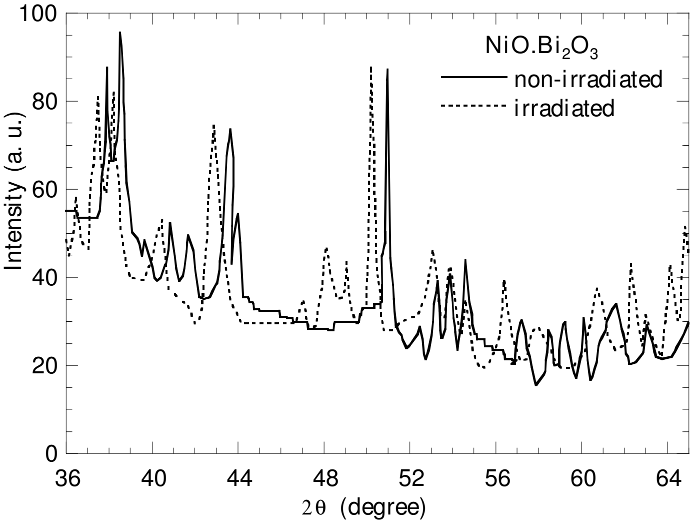


Fig. 5 – X-rays diffractograms for NiO · Bi_2O_3, before and after γ-irradiation.

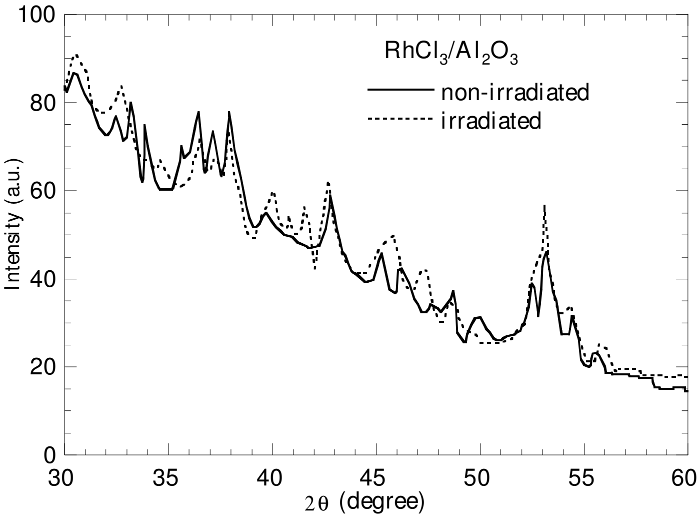


Fig. 6 – X-rays diffractograms for $RhCl_3/Al_2O_3$, before and after γ-irradiation.

CONCLUSIONS

The obtained experimental data lead to the following conclusions: the hydrogen quantity resulted from the catalyzed water radiolysis is 7-35 times greater with respect to the blank sample (without catalyst).

The hydrogen amount resulted from the catalyzed water radiolysis increases with the increase of the catalyst quantity, which is much more evident in the case of the system $RhCl_3$ / Al_2O_3.

The calculated radiochemical yield for hydrogen output in distilled water only (0.48) corresponds to those mentioned in the literature (0.45).

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