CATALYTIC PROPERTY OF DOUBLE LAYERED PEROVSKITES $A_2MM'O_6$ FOR RADIOLYTICAL SPLIT OF WATER

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Abstract: This paper deals with a study of water splitting by gamma rays in the presence of some double perovskites $A_2MM'O_6$ and also $Sr_2Fe_{1-x}Ta_{1+x}O_6$. The irradiation is performed using ^{60}Co as a source with $3 \cdot 10^4$ Ci activity and 8.3 kGy/h dose rate, which simulated the radioactive wastes, resulted from reprocessing of spent nuclear fuel elements much more active: 10^8-10^9 Ci. The stable products of radiolysis, as well as the other chemical species are measured by mass spectrometry. The calculated radiation yield (GH_2) generally decreases in the order: $Sr_2Fe_{1-x}Ta_{1+x}O_6$ (x=0.5; 0.4; 0.3; 0.1) > Ca_2AlTaO_6 > Sr_2AlTaO_6 > Ba_2AlTaO_6, under the given experimental conditions; the yield was higher in the presence of these catalysts than in their absence.

Keywords: catalytic effect, double perovskites, hydrogen production, water radiolysis.

Introduction

Photocatalytic water splitting in the presence of perovskites has received an extensive attention, as it can provide a clean and renewable source for hydrogen fuel. A variety of photocatalysts have been reported as active in water splitting process. In particular, 2D-layered photocatalysts are of great interest, because of the possibility to modify the chemical composition as well as microstructure by means of ion exchange or interaction.

Experimental results show that the 2D-layered perovskite oxide should be more favorable for water reducing due to the particular layered structure and the easy formation of large surface areas.

However, the application of these chemical compounds for pure water splitting was not successful, although a lot of cocatalysts were used, such as NiO, RuO_2 and Pt, to improve the activity of the 2D-layered photocatalyst [1].

Yao and Ye developed studies on $CsLaSrNb_2NiO_9$ and also on $K_2Sr_{1.5}TaO_{10}$ as photocatalysts in pure water splitting, even in the absence of any cocatalyst. Their studies pointed out that the new active catalysts for pure water splitting based on 2D-layered tantalate are stronger than those corresponding to niobate [2].

Li *et al.* investigated the photocatalytic properties of water splitting over a series of perovskite-type compounds $A_2MM'O_6$ (A=Ca, Sr, Ba; M=Ni, Co, Zn, Mg; M'= Mo, W). Although H_2 and O_2 evolution was observed under ultraviolet or visible light irradiation in the presence of CH_3OH or $AgNO_3$ as sacrificial reagents, it has been found that most of these compounds suffer instability in aqueous solution under light irradiation and only Ca_2NiWO_6 remained chemically stable [3].

The ideal catalyst should not react with the solvent used, resist to the action of light or nuclear radiations and did not catalyze the water decomposition at room temperature developing hydrogen.

The present paper is a continuation of some former studies regarding hydrogen output from water radiolysis in the presence of some solid catalysts. Here are investigated the catalytic properties of new double perovskites seria with the stoichiometry $A_2^{2+}M^{3+}M^{5+}O_6$ (A=Ca, Ba, Sr; M=Al; M'=Ta) and also $Sr_2Fe_{1-x}Ta_{1+x}O_6$ (x = 0.1; 0.3; 0.4; 0.5) in water splitting process, under gamma-rays irradiation emitted by a ^{60}Co source [4, 5].

Experimental Section

Sample Preparation and Characterization

Polycrystalline samples $A_2^{2+}M^{3+}M^{5+}O_6$ were synthesized by solid state reaction, from a stoichiometric mixture of ACO_3 ($SrCO_3$, $BaCO_3$), CaO, B_2O_3 (Al Fe) and Ta_2O_5 with a purity ranging between 99.99 and 99.999%. These carbonates and oxides were dried at 120ºC for 2 h before weighing. Afterwards, they were thoroughly mixed, placed in Al_2O_3 crucibles and heated at 950 ºC, for 6 h [6].

Other determinations showed that a thermal treatment at higher temperatures (~1500ºC) of these catalysts reduce their catalytic activity due to a higher crystallization degree. [7]

Structural properties

Structural characterization of these catalysts after the thermal treatment was accomplished using an Infrared spectrometer Jasco FT/IR–660 Plus. FT-IR spectra were registered between 4000 cm^{-1}-400 cm^{-1}, on the KBr tablets. Vibrational behavior of doubles perovskites is complex due to the fact that crystalline cell has two polyhedrons MO_6, each of them with metallic cations with different size and charge.

FT-IR spectra showed two strong adsorption bands, one in the 800-600 cm^{-1} domain due to the stretching vibration of M'O$_6$ polyhedrons and another one of low energy usually split at 450 cm^{-1} arrogated to the MO$_6$ polyhedrons distortion. Also, the formation of the perovskitic phase at 950 °C was noticed [8].

It is well known that the tolerance factor ŕ determines the crystal structure of perovskites AMO$_3$. Only for ŕ close to unity is a cubic perovskites structure obtained. For $f \neq 1$ a tilt and rotation of the oxygen octahedral is obtained, compensating for the misfit of the ionic radii of the involved A and M cations. The deviation of the tolerance factor from the ideal value $f=1$ can be used as a measure for the internal strain in perovskites induced by the different radii of the A and M cations. This can be seen from the definition of ŕ given by:

$$f = \frac{r_A + r_O}{\sqrt{2}(\langle r_M \rangle + r_O)}$$

(1)

where $\langle r_B \rangle$ denotes the average ionic radius for the ions on the M site. For $f<1$, the strain is compensated by a tilt and rotation of the oxygen octahedra. This results in a deviation of the M-O-M bond angles from the ideal value of 180°. For $0.96 \leq f \leq 1$ the connected pattern of the oxygen octahedral is rhombohedral, whereas it is orthorhombic for lower values of f. For $f>1.06$, a hexagonal structure is expected which is classified by the stacking sequence of the MO$_6$ octahedra [9, 10].

It was discussed the change of tolerance factor f and its influence on the structure for the system A$_2$AlTaO$_6$ (A=Ca, Ba, Sr) and Sr$_2$Fe$_{1-x}$Ta$_{1+x}$O$_6$ (x=0.1; 0.3; 0.4; 0.5). Tolerance factors were calculated using SPuDS simulation software.

Table 1

The tolerance factor of A$_2$MM'O$_6$ series (A= Ca, Ba, Sr)

Compound (t$_{sint}$)	f	Structure	Structure Lattice. parameters [Å]	Space group
Ca$_2$AlTaO$_6$ 950°C	0.9626	Monoclinic	a=5.3780 b=5.4154 c=7.6248	P$_{21/n}$
Ba$_2$AlTaO$_6$ 950°C	1.0790	Hexagonal	a=5.7155 c=13.9510	P6$_{3/mmc}$
Sr$_2$AlTaO$_6$ 950°C	1.0178	Cubic	a=7.795	Fm-3m
Sr$_2$Fe$_{1-x}$Ta$_{1+x}$O$_6$ 950°C	0.9825	Rhombohedric	a=5.6204 b=5.6161 c=7.9266	P$_{bmn}$

It can be notice that while Sr$_2$AlTaO$_6$ compound with ŕ=1.0178 is cubic, Ca$_2$AlTaO$_6$ compound with ŕ=0.9626 is strongly distorted forming a monoclinic system. In the case of Ba$_2$AlTaO$_6$ it can be considered that the size of Ba^{2+} cation will determine a strong deformation of the ideal crystallographic cell forming a hexagonal system.

Water decomposition

In the 30 ml glass vials different quantities of each catalyst were introduced and 5 ml of double distilled water were added. Each vial was tightly closed with rubber cork and outside paraffined to hinder the release of gaseous radiolysis product. These vials were γ-irradiated in different experimental conditions, under different dose rates, at IFIN-Bucharest. A blank sample for comparison was also prepared under the same conditions but without the addition of the catalyst.

The radiolysis products but also other chemical species having 14 and 28 mass numbers (corresponding to N and N$_2$) were analyzed by mass spectrometry, using an original connection device between the irradiated sample and the spectrometer, based on a metallic capillary.

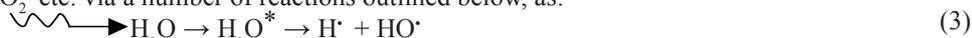Hiden Analytical mass spectrometer was first calibrated with the hydrogen resulted from a total chemical reaction:

$$Zn + 2 HCl_{dil} \rightarrow ZnCl_2 + H_2$$

(2)

This means that 1.08 g Zn corresponds to 0.01 mole H$_2$ which further correspond to peak intensity (in arbitrary units) of 1.58·10^7 in the mass spectrum, for the species having the mass number 2.

A vacuum of about 2·10^{-6} torr was reached inside of ionization chamber of mass spectrometer before each measurement, in order to avoid the contamination risk for the following vial with the chemical species of the previous sample. Computer plots the obtained experimental results as spectra, in the coordinates: Mass number = f (Peak intensity).

Results and discussion:

It's generally known that the radiolysis of water leads to the formation of different chemical species, such as: H_2, O_2, H_2O_2, $HO^{\bullet}$, O, $HO_2^{\bullet}$ etc. via a number of reactions outlined below, as:

$$\rightsquigarrow\rightarrow H_2O \rightarrow H_2O^* \rightarrow H^{\bullet} + HO^{\bullet} \tag{3}$$
$$\rightsquigarrow\rightarrow H_2O \rightarrow H_2O^+ + e^- \tag{4}$$
$$H_2O + e^- \rightarrow H_2O^- \tag{5}$$
$$H_2O^+ + H_2O^- \rightarrow 2H_2O^* \rightarrow 2H^{\bullet} + 2HO^{\bullet} \tag{6}$$
$$H^{\bullet} + H^{\bullet} \rightarrow H_2 \tag{7}$$
$$HO^{\bullet} + HO^{\bullet} \rightarrow HO_2^{\bullet} + H^{\bullet} \tag{8}$$
$$H^{\bullet} + O \rightarrow HO^{\bullet} \tag{9}$$
$$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \dots \tag{10}$$

Radiolytic yield of hydrogen, GH_2 (number of transformed or appeared molecules for 100eV absorbed energy, by γ-ray irradiation) was calculated using a formula deduced from the Henglein expression [11]:

$$G_{H_2} = \frac{b \cdot I_x}{D \cdot t \cdot \rho \cdot I_{et}} \cdot 9.66 \cdot 10^6 \tag{11}$$

where:

$D \cdot t = D_a$ – is the absorbed dose (1J/kg or $6.24 \cdot 10^{15}$ eV/g)   (12)
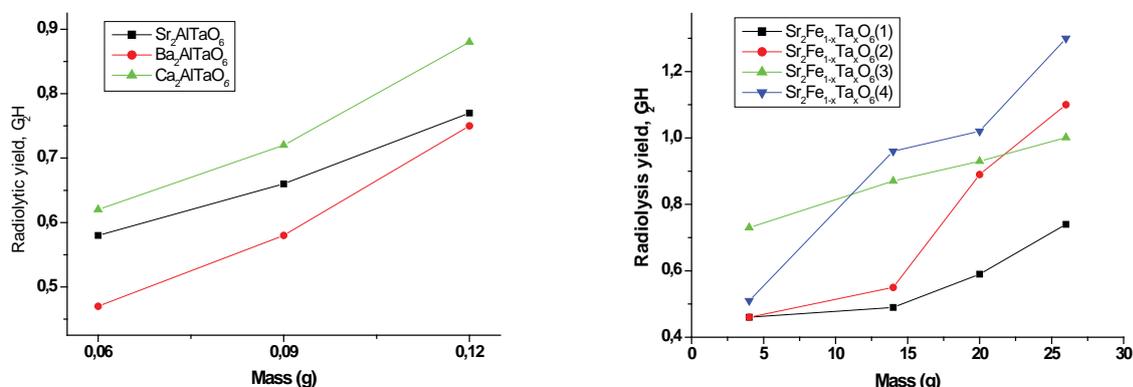
ρ - the density of irradiated material (g/cm^3),

b - hydrogen amount determined from the calibration of the mass spectrometer (mole H_2/1kg H_2O)

I_{et} - is peak intensity value of molecular hydrogen resulted from the mass spectrometer calibration reaction

I_x - is peak intensity value of molecular hydrogen resulted from the catalyzed water radiolysis

Several species ($H^{\bullet}$, $HO^{\bullet}$, $HO_2^{\bullet}$, and H_2O_2) were found in the mass spectra, but the radiolytic yield was determined only for molecular hydrogen.

The experimental results and also the catalysts efficiency in water radiolysis process were shown by the radiolytic yield values of the molecular hydrogen in several working conditions (Figures 1, 2).

Figure 1. Radiolytic yield vs catalysts mass (x = 0.1; 0.3; 0.4; 0.5).

Experimental data pointed out that radiolytic yields of molecular hydrogen increased when the absorbed dose (for a given quantity of catalyst) or perovskites mass (for the same dose) were increased.

The subsequent action of the gamma rays produces a radiolytical split of water, releasing a radiolytic yield GH_2 higher than that produced from pure water splitting in the absence of the catalyst (0.43), irradiated in the same conditions as the samples with catalyst.

Furthermore the FT-IR spectra were achieved on some of the catalysts before and after irradiation (Figure 3), to prove the catalytic effect of these solid masses in radiolytical split of water molecules. There were not observed any changes in their structure. FT-IR spectra were achieved in the same conditions, on tablets containing KBr dried for 24 h at 120°C.
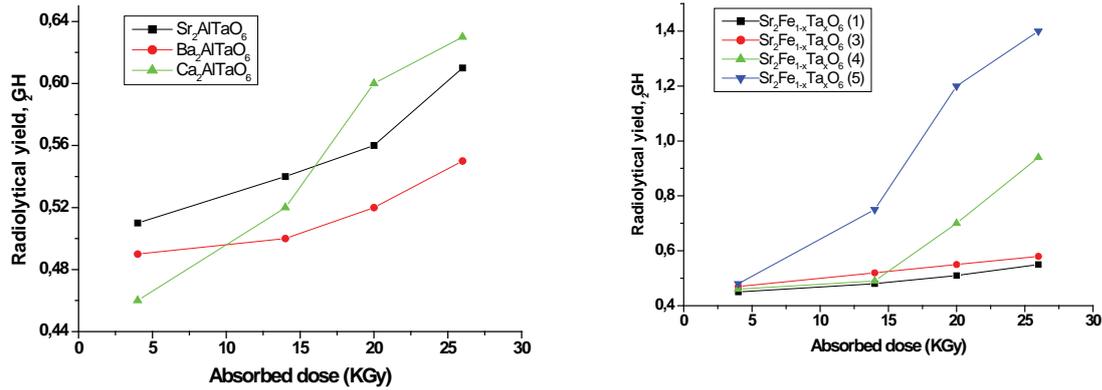
Figure 2. Radiolytic yield vs. absorbed dose (x = 0.1; 0.3; 0.4; 0.5).

Explaining the catalytic effect

Perovskite oxides contain large concentrations of oxygen vacancies, this being a consequence of the cation stoichiometries and valence.

It can be considered that the neutral water molecule will fill these oxide vacancies. Anionic vacancies ($V_O^{··}$) are acting as Lewis acid and the water molecules as Lewis base.

$$V_O^{··} + O_O^x + H_2O \leftrightarrow 2\ OH_O^· \tag{13}$$

From experimental data it was noticed that the double perovskite Ca_2AlTaO_6 had a higher catalytic effect comparing with Ba_2AlTaO_6 and Sr_2AlTaO_6. This might be explained on the base of ionic radii variation ($rCa^{2+} < rSr^{2+} < rBa^{2+}$). A smaller ionic radius will determine a higher number of anionic vacancy ($V_O^{··}$). Also, Ca^{2+} has a higher polarizing action on the water molecules, due to his smaller ionic radius.

The changes in stoichiometry that occur on annealing water in the perovskite structure can also be summarized:

$$A_2AlTaO_6 + x\ H_2O \rightarrow A_2AlTaO_{6-x}(OH)_{2x} \tag{14}$$
$$Sr_2Fe_{1-x}Ta_{1+x}O_6 + x\ H_2O \rightarrow Sr_2Fe_{1-x}Ta_{1+x}O_{6-x}(OH)_{2x} \tag{15}$$

In the case of $Sr_2Fe_{1-x}Ta_{1+x}O_6$ it might be consider that the catalytic effect increases with x value due of a greater number of anionic vacancies [12-16].
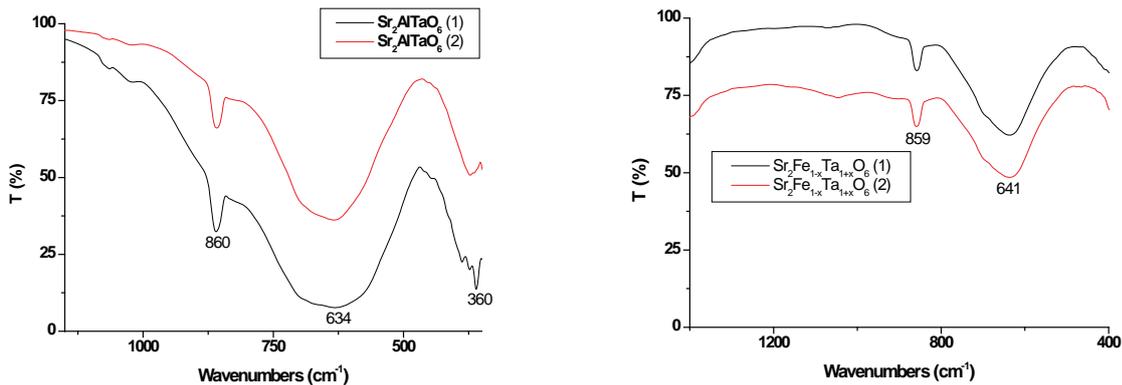

Figure 3. FTIR spectra of Sr_2AlTaO_6 and $Sr_2Fe_{1-x}Ta_{1+x}O_6$ (x=0.1), (1) before and (2) after irradiation.

Conclusion

The present paper has been directed towards the evaluation of the catalytic properties of some double perovkites A_2AlTaO_6 with different interlayer cations (A=Ca, Ba, Sr) and $Sr_2Fe_{1-x}Ta_{1+x}O_6$ (x=01; 0.3; 0.4; 0.5) for pure water splitting under γ-rays irradiation.

It was noticed that the double perovskites with A= Ca has a higher catalytic effect in water splitting and also the ones with $Sr_2Fe_{1-x}Ta_{1+x}O_6$ formula, where x=0.5.

Double perovskites $Sr_2Fe_{1-x}Ta_{1+x}O_6$ have a more important catalytic effect comparing with A_2AlTaO_6 (A=Ca, Ba, Sr).

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