

Hydrogen yield from water radiolysis in the presence of zeolites

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Abstract: This paper reports a study of the decomposition of water by gamma radiolysis in the presence of zeolites ZSM-5, SAPO-5, and MOR. The irradiation is performed using ⁶⁰Co as a source with 1.12×10^{15} Bq activity at a 8.3 kGy/h dose rate. The stable products of radiolysis as well as the other chemical species are measured by mass spectrometry. The calculated radiation yield (G_{H_2}) generally decreases in the order: H-ZSM-5 > Na-ZSM-5 > H-SAPO-5 > MOR under the given experimental conditions; the yield is higher in the presence of these catalysts than in their absence.

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1 Introduction

Of all the radiation-chemical reactions that have been studied on aqueous solutions, perhaps the most important reaction is the decomposition of pure water itself. The hydrogen yield from water radiolysis has been investigated using various β , γ , and neutron irradiation sources, and under different experimental conditions [1 – 5]. The possibility of using the radiation emitted by unstable fission products contained in spent nuclear fuel elements for the low cost production of hydrogen via catalyzed water radiolysis, has also

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been reported [6 – 8].

Enhanced H₂ production from water radiolysis is observed in the presence of some oxides, zeolites, and supramolecular compounds.

This paper reports the study of the hydrogen yield from water radiolysis utilizing zeolites as catalysts. The source of γ radiation is a ⁶⁰Co radionuclide having an activity of 1.12×10^{15} Bq. This source may mimic radioactive wastes with higher activity, which could be used to catalyze the radiolysis of water for hydrogen production. The radiolysis products are analyzed by a new method based on mass spectrometry [9, 10].

2 Experimental

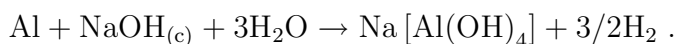
Samples for the catalyzed radiolysis of water were prepared as follows: 0.1 – 0.5 g of a solid, powdered catalyst and 10 mL of distilled water were placed in 30 mL vials. The vials were tightly sealed with a rubber cork and coated with paraffin. A blank sample for comparison was also prepared under the same conditions but without the addition of the catalyst.

All samples were placed in a circle ($\Phi = 30$ cm) around the ⁶⁰Co γ source ($\Lambda = 1.12 \times 10^{15}$ Bq, 8.3 kGy·h⁻¹ dose rate) inside the irradiation device. The whole irradiation device was immersed in water, and the irradiations were performed for different time intervals (24, 48, 72, 96, 120 h).

The stable radiolysis products such as H₂ and O₂ (partially), as well as other chemical species HO•, N, and N₂, were analyzed using mass spectrometry. The samples were connected to a VESTEC mass spectrometer using a device with a chromatographic syringe needle. The base of the needle was attached to the entrance of the device, and the top of the needle was pushed into the rubber cork of vials. Before any determination, the mass spectrometer was evacuated to 10⁻² Pa.

The experimental data processed by the computer were plotted using coordinates of peak intensity (arbitrary units) versus the mass number of detected chemical species.

The mass spectrometer was calibrated with a known amount of hydrogen produced by the following chemical reaction



A given amount of aluminium powder and 20 mL of a 40% NaOH solution were placed in a vial. The vial was hermetically sealed.

The zeolites used [11] as catalysts for the water radiolysis did not react with or dissolve in the solvent. The crystalline structure of zeolites did not change during irradiation; this fact was proven by X-ray diffraction.

The main properties of the zeolites used in this study are shown in Table 1.

3 Results and discussion

The results acquired are summarized in Table 2. The radiolysis process may be represented as follows [12 – 14]:



The radiation yield (G_{H_2}) is calculated by considering the amount of hydrogen produced in the calibration reaction mentioned in the experimental.

$3.34 \cdot 10^{-2} \text{g H}_2 / 10 \text{ mL H}_2\text{O} \rightarrow 1.67 \text{ moles H}_2 / 1 \text{ kg H}_2\text{O} \rightarrow \text{peak intensity: } 7883840$ (arbitrary units).

For the case of a 24 h irradiation, the radiation dose is:

$$8300 \times 24 = 1.99 \cdot 10^5 \text{ J/kg H}_2\text{O} \quad (9)$$

and the radiation yield can be calculated as follows:

$$G_{\text{H}_2} = \frac{1.67 \times 6.023 \cdot 10^{23} \cdot I}{1.99 \cdot 10^5 \times 6.24 \cdot 10^{16} \cdot 7.88 \cdot 10^6} = 1.3 \cdot 10^{-6} \cdot I \quad (10)$$

Here "I" refers to the peak intensity of the corresponding mass number in a measured sample.

Table 2 shows peak intensity values for the main species with the following mass numbers: 2, 14, 16, 17, 28, and 32.

The peak intensity values for HO^\bullet vary around a medium value that is close to the corresponding peak intensity for the comparison sample (10 mL H_2O), when irradiated for 24 hours. On the other hand, the peak intensity values for hydrogen are much higher in the catalyzed samples than in the comparison samples. Thus, we can conclude that the hydrogen molecules detected result mostly from their production by water radiolysis and are not produced by ionization inside the mass spectrometer. Also, another species with the same mass number 17, namely NH_3 , has no chance of being produced in the irradiation system due to the more highly energetic conditions necessary to synthesize the ammonia.

The N and N_2 species (determined by mass spectrometry) exist together with oxygen resulting partially from the composition of atmospheric air in the 10 mL water sample in each closed vial. Another part of the oxygen detected (as O and O_2) comes from radiolysis of water, and for this reason the quantities of these chemical species detected in the mass spectrograms represent global values from both air composition and radiolysis.

The radiolytical split of water in the presence of a catalyst can be explained by a mechanism based on surface molecular interactions [15]. As a consequence of adsorption and penetration into the pores of the catalyst, the water molecules get closer to the negative part of the electric dipole on the zeolite surface. Thus, the O – H bond becomes weaker. The subsequent action of the gamma rays produces a radiolytical split of water, releasing a quantity of a hydrogen greater than that produced in the absence of the catalyst.

4 Conclusion

From the experimental data presented, we conclude the following:

- (1) The radiation yield of hydrogen (G_{H_2}) increases with an increasing amount of catalyst.
- (2) For a given amount of zeolite, the amount of hydrogen produced increases with increasing irradiation time and absorbed energy during the water radiolysis process. In both cases, the increase in the amount of hydrogen is random, not exponential, linear, etc.. This is probably due to the loss of gas through the walls of the experimental equipment, considering that hydrogen can even diffuse through a glass soldered seal.
- (3) Under the given experimental conditions, the amount of hydrogen produced decreases as follows: H-ZSM-5 > Na-ZSM-5 > H-SAPO-5 > MOR showing a dependence upon the geometry of the adsorption surface and the pore size of the catalyst.

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Zeolite type	Framework density (T/1000 Å ³)	Free volume (cc/g)	Crystallization structure	Pore structure (channel system)
H-MOR	17.2	0.20	Orthorhombic	One dimensional intersecting 8- and 12- member rings (6.5×7.4 and 2.6×5.6 Å)
H-ZSM-5	17.9	0.10	Orthorhombic	Three dimensional intersecting 10-member rings (5.2×5.5 Å)
H-SAPO-5	17.5	0.16	Hexagonal	One dimensional intersecting 12- member rings (7.3×7.3 Å)

Table 1 Some crystalline network parameters of studied zeolites.

Sample No.	Catalyst	Irradiation time (h)	Amount of catalyst (g)	H ₂	O	HO•	N	N ₂	O ₂	G _{H₂} *
1	H-ZSM-5	24	0.1	188050	8750	28750	12300	70050	81500	1.92
2		24	0.2	195000	8450	27900	13350	73450	80100	2.00
3		24	0.3	195900	9450	30500	12440	68750	69500	2.01
4		24	0.4	235200	11650	38200	9450	87700	62000	2.49
5		24	0.5	256450	23050	15600	9030	46070	72500	2.61
6	H-SAPO-5	24	0.1	189000	11450	16750	39300	168800	94400	1.94
7		24	0.2	176900	8600	17150	25000	132450	96120	1.81
8		24	0.3	184350	11650	16800	34590	158000	89320	2.09
9		24	0.4	191500	11200	15800	39850	132500	76600	1.96
10		24	0.5	194050	13100	16240	41700	173200	105900	1.99
11	H-MOR	24	0.1	97200	9100	28000	47300	87100	68700	1.02
12		24	0.2	97350	10300	21500	24800	119800	61600	0.98
13		24	0.3	97220	9700	25060	36900	93700	75100	0.97
14		24	0.4	98800	9000	16650	25100	109700	70350	1.01
15		24	0.5	97600	8150	17350	20450	106000	71200	0.98
16	Na-ZSM-5	24	0.1	183950	11500	46700	38100	170100	94500	1.85
17		24	0.2	198850	17200	56100	83000	180600	98600	2.03
18		24	0.3	209700	15060	46300	36450	161800	95500	2.09
19		24	0.4	239860	14400	48450	21700	117150	89900	2.44
20		24	0.5	248200	16260	45600	33000	200760	99020	2.54
21	H-SAPO-5	48	0.1	264800	6400	18600	19200	107300	90900	1.35
22		72	0.1	407950	10100	13600	36700	108150	89000	1.36
23		96	0.1	585700	16060	26500	22700	108800	92000	1.50
24		120	0.1	801600	19400	19200	20100	88300	83000	1.65
25	Na-ZSM-5	48	0.1	283950	11400	15500	38100	170100	95900	1.45
26		72	0.1	457600	16100	12850	19800	111750	90200	1.56
27		96	0.1	705500	38000	15600	33600	116050	92760	1.80
28		120	0.1	1089600	31500	19000	26400	112450	96300	2.23
29	H-MOR	48	0.1	210600	16050	29500	23450	112600	93600	1.07
30		72	0.1	415950	18100	40450	8850	104000	90100	1.40
31		96	0.1	697500	18600	49400	31050	107650	98410	1.73
32		120	0.1	843700	26700	46200	22500	127400	96500	1.75
33	H-ZSM-5	48	0.1	337050	36800	82500	55600	108950	87900	1.72
34		72	0.1	516000	26600	64900	43350	77000	68700	1.78
35		96	0.1	817900	31050	39500	43600	112400	85900	2.09
36		120	0.1	1140100	17300	37450	40100	91600	89300	2.33
37	Uncatalyzed irradiated water	24	-	49900	4850	26300	24000	113900	51000	0.48
Radiation yield found in the literature [12]										0.45

*Yield unit: H₂ molecules / 100 eV

Table 2 Peak intensities (in arbitrary units) of the main species and radiation yields (G_{H₂}) for the given experimental conditions.