

Investigation of Radiation-Induced Heterogeneous Processes in the NaX + H₂O System by Electron Paramagnetic Resonance Spectroscopy

Teymur Agayev

agayevteymur61@gmail.com

Ministry of Science and Education

Fethullah Chichek

Ministry of Science and Education

Research Article

Keywords: NaX zeolite, gamma irradiation, electron paramagnetic resonance, heterogeneous radiolysis, hydrogen production

Posted Date: October 22nd, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-11242382/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Additional Declarations: No competing interests reported.

Abstract

This study investigates radiation-induced heterogeneous processes in the NaX zeolite–H₂O system using Electron Paramagnetic Resonance (EPR) spectroscopy. Radiation-induced paramagnetic centers and free radicals were characterized using Electron Paramagnetic Resonance (EPR) spectroscopy, while the molecular hydrogen formed was analyzed by gas chromatography. It was established that an increase in the water content leads to a decrease in the concentration of hole centers in NaX zeolite and an increase in the concentrations of H and OH radicals. The kinetics of the accumulation of these species were studied, and their radiation-chemical yields were determined. Based on the experimental observations, a reaction mechanism describing charge carrier localization, water radiolysis, and molecular hydrogen formation is proposed. The findings demonstrate that NaX zeolite provides an efficient catalytic environment for radiation-assisted water splitting and hydrogen production while contributing to a better understanding of radiation-catalytic processes occurring in heterogeneous systems.

Introduction

The kinetics of molecular hydrogen accumulation on the NaX surface at different temperatures was investigated. Using electron paramagnetic resonance (EPR) spectroscopy, the formation processes of paramagnetic defects and free-radical products were studied in NaX zeolite + H₂O systems with different water contents irradiated with γ -rays at **T = 77 K**. It was established that an increase in the water content leads to a decrease in the concentration of hole centers in the NaX zeolite, while simultaneously increasing the concentrations of H• and •OH radicals. The accumulation kinetics of the hole centers were investigated, and their radiation-chemical yields were calculated. A reaction mechanism that accounts for the experimental results was proposed.

In the selection of solid catalysts to be used in radiation-chemical processes, it is of great importance to investigate the fundamental principles governing their radiation-catalytic effects and to elucidate the mechanisms of radiation-chemical transformations of molecules in heterogeneous systems. In particular, in systems where water is confined by solid surfaces and porous structures, the electrons, positive charge carriers, and radical species generated by ionizing radiation may undergo reaction pathways that differ from those occurring during homogeneous water radiolysis [5, 6, 18, 19].

Studies published in recent years have demonstrated that the radiation-catalytic effect of oxide catalysts on water radiolysis varies depending on the catalyst composition, the physicochemical properties of the surface, and the process conditions [5, 14]. Investigations of water radiolysis in the presence of oxides and other porous solid surfaces have revealed the influence of surface-generated active centers and charge carriers on the formation and recombination processes of radiolytic products [5, 6, 9, 14].

Radiation-catalytic decomposition of substances in the presence of various oxide compounds has emerged as a new research direction in the fields of radiation catalysis, surface physics and chemistry, and radiation materials science [5, 14]. These studies are of great importance for understanding the

nature of the radiation-catalytic effects of oxide compounds and for enabling the effective utilization of both the radiation and thermal components of nuclear energy in chemical transformations. However, in radiolytic processes occurring on solid surfaces and within porous structures, the localization of charge carriers, their interactions with surface defects, and their involvement in the decomposition of adsorbed water molecules are strongly dependent on the physicochemical properties of the system [6, 7, 10, 17].

However, the general principles governing radiation-catalytic effects and the scientific basis for the selection of suitable catalysts for radiation-catalytic transformations have not yet been fully established. In particular, the confinement of water molecules within microporous structures such as zeolites can significantly affect the mobility, trapping, and recombination kinetics of radiation-generated H atoms and other radical species [7, 17]. To elucidate the mechanisms of defect formation in zeolites and the transfer of energy from the zeolite framework to molecules adsorbed on the surface, defect formation on the zeolite surface and the transformation processes of water were investigated using electron paramagnetic resonance (EPR) spectroscopy. EPR spectroscopy is an effective technique for the direct characterization of radiation-induced paramagnetic centers, particularly radical species such as H atoms and $\bullet\text{OH}$ radicals [7, 9, 17].

Previous studies have demonstrated that EPR spectroscopy is an effective method for investigating the formation and transformation processes of reactive intermediate radical species and, thereby, for elucidating the characteristics of radiation-induced heterogeneous transformations of water in the presence of various oxide catalysts [7, 9, 14, 17]. Studies of zeolite–water systems have also shown that H atoms formed as a result of water radiolysis can be stabilized within zeolite frameworks or porous structures and can participate in recombination or desorption processes as the temperature increases [7, 17].

In the present study, the kinetics of molecular hydrogen accumulation at different temperatures were investigated. In addition, the accumulation kinetics of paramagnetic centers (PCs) and radical products in the NaX zeolite + H_2O system at **T = 77 K** were investigated in detail using EPR spectroscopy under conditions of varying amounts of water adsorbed on the surface.

Experimental Section

The general flowchart of the experimental procedure employed in this study is presented in Fig. 1. The experimental study consisted of NaX zeolite activation, water adsorption, gamma irradiation, and EPR analyses. The detailed experimental conditions are described below.

In the experimental procedure, **NaX-type zeolite** with a **$\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 2.5** was used. The zeolite samples were initially subjected to heat treatment at **873 K** in an oxygen atmosphere for **48 h**. Subsequently, the samples were activated at **823 K** for **8 h** by alternately maintaining them under **1 h of vacuum ($P \approx 10^{-2}$ Pa)** and **1 h of oxygen atmosphere**.

Following activation, the samples were transferred into quartz-glass ampoules and subsequently subjected to additional heat treatment at **673 K** under a vacuum of $P \approx 1.33 \times 10^{-3} \text{ Pa}$. Water adsorption was carried out using a **volumetric adsorption apparatus**.

The samples were irradiated with ^{60}Co **gamma rays** at a dose rate of 1.2 Gy s^{-1} over the temperature range of **673–873 K** and also at **77 K**.

Electron paramagnetic resonance (EPR) spectra were recorded at **77 K** using an **EMX-plus EPR spectrometer** (Bruker). The spectrometer operated in the **X-band** at a frequency of approximately $\nu \approx 9.8 \text{ GHz}$, with a linear magnetic field sweep range of **0–6000 G** and a magnetic field modulation frequency of **100 kHz**.

The samples were placed in specially designed **EPR quartz tubes with an inner diameter of 4 mm**. The maximum magnetic field modulation amplitude was set to **20 G**; however, to obtain accurate spectra, the modulation amplitude was optimized according to the linewidth of the spectrum under investigation. Mn^{2+} ions in MgO were used as a reference standard. The concentrations of the paramagnetic centers (PMs) were determined according to a previously reported quantitative EPR method [20].

Results and Discussion

To elucidate the fundamental characteristics of the catalytic decomposition of water in the presence of NaX zeolite, the kinetics of molecular hydrogen formation were investigated at different temperatures. The catalytic activity of the zeolite was investigated in a static system. The composition of the gas-phase products was analyzed using an **Agilent 7890 gas chromatograph**.

Figure 2 shows the characteristic kinetic curves for molecular hydrogen formation during thermocatalytic and radiation-thermocatalytic water decomposition under static conditions over the temperature range of 673–873 K. The formation of H_2 under irradiation in such zeolite–water systems has also been reported previously, and the amount of hydrogen formed has been shown to depend on the structural characteristics of the system and the radiolysis conditions [3, 12]. In porous or surface-confined water systems, surface interactions and radiation-generated intermediate species can significantly influence the pathways of H_2 formation [5, 10].

The process rates and radiation-chemical yields of molecular hydrogen were determined from these curves. As a first approximation, the contribution of radiation to the radiation-thermal processes was calculated using the following equation:

where:

$$W(\text{H}) = W(\text{H}) - W(\text{H})$$

- **$W_{\text{rad}}(\text{H}_2)$** : the rate of molecular hydrogen formation resulting from the radiation contribution,

- **Wrt(H₂)**: the rate of molecular hydrogen formation during radiation-thermocatalytic processes,
- **Wter(H₂)**: the rate of molecular hydrogen formation during thermocatalytic water decomposition.

Comparison of the molecular hydrogen yields in radiation-induced heterogeneous processes occurring in the NaX + H₂O system over the temperature range of **300–873 K** demonstrates that increasing temperature significantly accelerates heterogeneous water radiolysis. This temperature dependence is consistent with heterogeneous radiolysis systems in which the reactive intermediates generated by radiation must be considered in conjunction with thermal mobility and surface reactions [5, 6, 10].

Under these conditions, the radiation-chemical yield of molecular hydrogen, **G(H₂)**, increases approximately linearly from **0.65 molecules/100 eV at 300 K** to **9.1 molecules/100 eV at 873 K**. The temperature dependence of the process rate was evaluated using the **lgW = f(1/T)** relationship, and the corresponding activation energies were calculated. The activation energies (**E_a**) for the radiation-thermocatalytic and thermocatalytic processes were determined to be **38.5 kJ mol⁻¹** and **59.2 kJ mol⁻¹**.

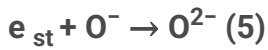
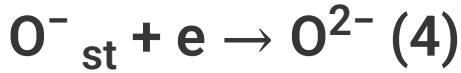
The results demonstrate that the activation energy of thermocatalytic water decomposition in the presence of NaX zeolite is higher than that of the radiation-thermocatalytic process. The generation of electrons and other short-lived reactive species during water radiolysis by irradiation may enable reactions occurring on solid surfaces to proceed through reaction pathways that differ from those of conventional thermal processes [5, 18, 19]. In heterogeneous radiolysis systems in particular, surface properties, pore structure, and the localization of charge carriers are considered among the key factors governing the transfer of radiation energy to chemical conversion [5, 6].

The underlying reason for this behavior may be that, in radiation-thermocatalytic processes, not only thermally active surface centers but also radiation-induced active surface centers and secondary electrons generated by gamma irradiation participate in the reaction. It is known that ionizing radiation generates low-energy secondary electrons, which can contribute to radiation-chemical processes through energy transfer within the solid structure [19]. These high-energy or radiation-generated active species may facilitate molecular hydrogen formation by enabling the reaction to proceed through a lower effective energy barrier. In contrast, in purely thermal processes, a higher energy barrier must be overcome for the reaction to proceed; therefore, a higher activation energy is expected. The experimentally determined activation energy of **38.5 kJ mol⁻¹** for the radiation-thermocatalytic process in the NaX–H₂O system, which is lower than the **59.2 kJ mol⁻¹** determined for the thermocatalytic process, suggests that irradiation provides an additional reaction pathway alongside the thermal process.

Formation of Paramagnetic Defects in the γ-Irradiated NaX Zeolite + H₂O System

The formation processes of paramagnetic defects in the γ-irradiated NaX zeolite + H₂O system were investigated using electron paramagnetic resonance (EPR) spectroscopy. Previous studies have demonstrated that paramagnetic centers and radiation-induced radical species formed in zeolitic structures under the influence of ionizing radiation can be characterized by EPR spectroscopy [1, 7, 17].

The generation and localization of unstable charge carriers within the crystal structure under the influence of gamma photons can be described by the following schematic mechanism:



Here, O^- and e^- denote holes and electrons, respectively, whereas O^-_{st} and e^-_{st} represent their localized (trapped) states. L_D and L_A denote electron-donor and electron-acceptor centers, respectively, in the zeolite structure, while k_i represents the rate constants of the corresponding reactions. The localization of radiation-generated electrons and holes in zeolites by structural defects, heteroatom environments, and surface centers is one of the fundamental processes governing the radiation chemistry of the solid structure. The trapping and recombination of such charge carriers can directly influence the manner in which radiation energy is transferred to chemical transformations [1, 7, 17].

In the presence of water molecules adsorbed on the zeolite surface, an additional process emerges that competes with Reactions (2) and (3), which describe the localization of unstable charge carriers. In this process, the unstable charge carriers interact with the adsorbed water molecules, resulting in the decomposition of water:



The most important evidence supporting this mechanism is the decrease in the signal intensity attributed to hole centers in the EPR spectrum of the $\text{NaX} + \text{H}_2\text{O}$ system, accompanied by the appearance of a doublet signal corresponding to the atomic hydrogen radical ($\text{H}\cdot$). The formation and subsequent trapping of H atoms during the radiolysis of confined or zeolite-framework water have also been previously observed, demonstrating the influence of the microporous environment containing water on the radiation-chemical process [7, 17].

At low water contents in the $\text{NaX} + \text{H}_2\text{O}$ system, the catalytically active sites of the zeolite are only partially occupied by water molecules. Therefore, a fraction of the unbalanced charge carriers still becomes localized according to reactions (2) and (3), forming paramagnetic centers. However, the changes observed in the parameters of the EPR line corresponding to the V_2 centers ($\Delta H = 1.4 \text{ mT}$ and g

= 2.0071) are considered to result from the interaction between the hole centers and water molecules ($V_2 \cdots H_2O$).

Reactions of charge carriers competing with water molecules and the resulting formation of radical species such as $H\cdot$ are consistent with the radiolysis behavior observed in porous solid–water systems [6, 7, 9, 17]. In particular, the formation, trapping, and kinetic behavior of H atoms in wet zeolites have been investigated in detail previously [17]. In zeolite samples dehydrated at high temperatures, defective aluminum–oxygen and silicon–oxygen polyhedra are present that can trap the radiolysis products of water. The role of such structural defects in the stabilization of radiation-induced paramagnetic species has previously been demonstrated in EPR studies of zeolite systems [1, 7].

At low water contents ($mH_2O < 1.103 \mu\text{mol/g}$), the absence of the line attributed to OH radicals in the EPR spectrum of the NaX + H_2O system (Fig. 3) can be explained by the trapping of these radicals by the aforementioned polyhedra.

Effect of Water Content on EPR Signals and Radiation-Chemical Yields

As the water content (mH_2O) in the system increases, the EPR spectrum of the NaX + H_2O system becomes more complex, and when $mH_2O > 3 \times 10^3 \text{ mmol/g}$, the spectrum resembles the EPR spectra observed during the γ -radiolysis of water in the presence of NaA, CaA, NaX, and CaX zeolites. In Fig. 3, curve (1) represents the low water content, whereas curve (2) represents the high water content. Previous studies have shown that an increase in water content in zeolite–water systems can alter the distribution of radiolysis products and paramagnetic centers [7, 9, 17].

The complex line located at the center can be considered as the superposition of four components (a' , a , b , and c). The a' and a components ($g \approx 2.0080$, $A = 4.2 \text{ mT}$) correspond to OH radicals. The narrow lines designated as b and c ($g \approx 2.0020$) are attributed to trapped electrons [9, 17]. The c component of the spectrum corresponds to the line observed at low water contents in the NaX + H_2O system and most likely originates from a paramagnetic center associated with the zeolite. Under the condition $\mu H_2O = 1.65 \times 10^4 \mu\text{mol g}^{-1}$, the accumulation kinetics of $\cdot OH$, $H\cdot$, and V_2 centers were investigated. Based on the kinetic curves, the radiation-chemical yields per 100 eV of energy absorbed by the system were calculated. Accordingly:

$$\bullet G(\cdot OH) = 0.71$$

$$\bullet G(H\cdot) = 0.35$$

$$\bullet G(V_2) = G(\text{Hole Center}) = 0.67$$

In the initially completely dehydrated NaX zeolite, the radiation-chemical yield of hole centers was found to be $G(\text{Hole Center}) = 1.30$. Using the same method, the radiation-chemical yields of hydrogen atoms and hole centers at different water contents were also calculated. As shown in Fig. 4, with increasing accumulation of hydrogen atoms ($H\cdot$), the radiation-chemical yield $G(\text{Hole Center})$ decreases. This result

can be regarded as important evidence directly indicating that, in the NaX + H₂O heterogeneous system, water molecules undergo decomposition with the participation of unbalanced charge carriers. The formation of H atoms during the radiolysis of water confined in zeolites and their stabilization within the solid structure have been reported previously, and the observed trend is qualitatively consistent with these studies [7, 17].

Based on reactions (1)–(6) and applying the steady-state approach, the following expression was obtained:

$$1/G(O^-_{ST}) = k_6[H_2O_S]/k_2G_{HH}[L_D] + 1/G_{HH}(k_5[e_{ST}]/k_2[L_D] - k_3[L_A]/k_4[O^-_{ST}])$$

- **G_{HH}** is the initial radiation-chemical yield of unstable charge carriers;
- **H₂O** denotes water molecules adsorbed on the zeolite surface;
- **LD** and **LA** denote electron-donor and electron-acceptor centers, respectively;
- **k_i** denotes the rate constants of the corresponding reactions.

As can be seen from the above equation, an increase in the amount of adsorbed water (H₂O) leads to a decrease in the radiation-chemical yield **G(O⁻)** of localized hole centers. This result is qualitatively consistent with the experimental findings. Similarly, the effect of adsorbed water on the formation and trapping of radiation-generated charge carriers and H atoms in zeolites has been investigated previously [7, 17].

Recombination of H Atoms and Formation of Molecular Hydrogen

During low-temperature radiolysis (**T = 77 K**), hydrogen atoms may not only become stabilized but may also recombine to form molecular hydrogen. However, in porous and zeolitic environments, the behavior of H atoms is more complex than can be explained solely by H–H recombination. Previous EPR and pulse-radiolysis studies have demonstrated that, in hydrated zeolites, radiolytic H atoms can originate from both adsorbed water and the solid matrix and can be trapped by defects within the solid structure [17].

In this context, two principal pathways for the behavior of H atoms can be considered:



Here, process (7) represents the stabilization of H atoms by active or defect centers within the zeolite structure, whereas process (8) represents the formation of molecular hydrogen through the recombination of two H atoms.

When the system is heated to room temperature ($T = 300\text{ K}$), the $\text{H}\cdot$ and $\cdot\text{OH}$ radicals disappear completely. The main reactions responsible for the disappearance of these radicals with increasing temperature can be expressed as follows:



In addition to these reactions, an increase in temperature may also facilitate the mobilization of H atoms previously stabilized within the zeolite structure, enabling them to react with one another or with other reactive centers in the solid matrix. Chemerisov et al. demonstrated that the kinetics of H atoms in porous solids differ from those in bulk ice, with interactions with metastable defects in the solid structure being particularly important in zeolites [17].

To elucidate the mechanism of molecular hydrogen formation, the ampoules were heated to room temperature ($T = 300\text{ K}$) after recording the EPR spectra, and the amount of molecular hydrogen contained in the ampoules was determined chromatographically. Previous studies have also demonstrated that H_2 formation as a result of γ -irradiation in zeolite–water systems depends on the water loading, and that zeolite–water interactions can affect H_2 formation [3].

Based on the kinetic curves, the radiation-chemical yields of molecular hydrogen at $\mu\text{H}_2\text{O} = 5$ and $100\text{ }\mu\text{mol/g}$ were determined to be $G(\text{H}_2) = 0.013$ and 0.065 , respectively. As can be seen, the relationship $2G(\text{H}_2) \geq G(\text{H})$ is satisfied in the system.

The relationship between the yields of H_2 and H radicals observed during the low-temperature radiolysis of water in the presence of NaX indicates that a substantial fraction of the hydrogen atoms formed at $T = 77\text{ K}$ undergo recombination to form molecular hydrogen (Eq. 8), while only a small fraction becomes stabilized according to Eq. (7). However, the reaction of H atoms with defects in the solid structure should also be taken into account when quantitatively evaluating this interpretation, since a significant fraction of H atoms in hydrated zeolites has been shown to be trapped by matrix defects [17].

This observation is further supported by the non-stoichiometric relationship between the yields of H and OH radicals observed during the radiolysis of adsorbed water at $T = 77\text{ K}$ and $\mu\text{H}_2\text{O} = 1.65 \times 10^4\text{ }\mu\text{mol/g}$ (Fig. 4). Previous experimental studies have demonstrated that H_2 production in zeolite–water systems can vary depending on the water loading and the organization of water within the zeolite structure [3].

When the experimental findings presented above, the EPR analyses, and the kinetics of molecular hydrogen formation are considered together, the reaction mechanism proposed for the radiation-catalytic process occurring in the NaX– H_2O system under γ -irradiation is schematically presented in Fig. 5. The proposed mechanism provides an integrated description of the generation and localization of nonequilibrium charge carriers induced by γ -irradiation, the radiolysis of adsorbed water molecules, the formation of $\text{H}\cdot$ and $\cdot\text{OH}$ radicals, and the subsequent production of molecular hydrogen. The formation

of H atoms as a result of the radiolysis of adsorbed water in zeolites and the trapping of these species within the solid structure have previously been demonstrated using EPR and time-resolved radiolysis techniques [17]. Therefore, the mechanism presented in Fig. 5 is not based on a single reaction pathway but rather on a sequence of consecutive and competing processes: **charge-carrier generation → localization/trapping → interaction with adsorbed water → formation of H• and •OH radicals → H• recombination → H₂ formation**. The previously reported dependence of H₂ formation in zeolite–water systems on the water content and the strength of zeolite–water interactions further supports the evaluation of the proposed mechanism in conjunction with the experimental results [3].

Conclusion

Thus, in this study, the radiation-induced heterogeneous processes occurring in the NaX zeolite–H₂O system were investigated in detail by evaluating Electron Paramagnetic Resonance (EPR) spectroscopy together with molecular hydrogen formation measurements. The results obtained demonstrate that the amount and physicochemical state of adsorbed water are among the most important parameters determining the formation of radiation-induced reactive species.

EPR analyses revealed the formation of hole centers, trapped electrons, H• atoms, and •OH radicals in the NaX structure as a result of γ-irradiation. With increasing amounts of adsorbed water, the radiation-chemical yield of hole centers decreased, whereas the formation of H• and •OH radicals increased markedly. This indicates that radiation-generated charge carriers react with adsorbed water molecules rather than becoming trapped within the zeolite structure, thereby promoting water decomposition.

Hydrogen formation experiments demonstrated that radiation-thermocatalytic water splitting is significantly accelerated with increasing temperature. At the same time, the lower activation energy calculated for the radiation-assisted process compared with the thermocatalytic process alone confirms that the active surface centers and secondary electrons generated by gamma irradiation facilitate the reaction and accelerate hydrogen formation.

In accordance with the experimental findings, the proposed reaction mechanism successfully explains the formation and trapping of non-equilibrium charge carriers, their transfer to adsorbed water molecules, radical formation, and molecular hydrogen production. The consistency between the EPR results and hydrogen production data indicates that the radiation-induced heterogeneous reactions occurring on the NaX surface predominantly proceed through a radical mechanism.

In conclusion, NaX zeolite provides an effective catalytic environment for radiation-assisted water splitting and hydrogen production. This study not only contributes to the understanding of radiation-chemical mechanisms in NaX zeolite but also provides a scientific basis for the development of next-generation hydrogen production technologies employing ionizing radiation in combination with heterogeneous catalysis.

Declarations

Author Contribution

TA developed the scientific framework of the study and conducted the experimental investigations in collaboration with FC. TA established the initial structure of the manuscript, while FC conducted the necessary literature review and contributed to the completion and refinement of the manuscript. FC also prepared and formatted the figures and graphical materials.

References

1. Danilczuk M, Pogocki D, Lund A, Michalik J (2006) EPR and DFT Study on the Stabilization of Radiation-Generated Methyl Radicals in Dehydrated Na-A Zeolite. *J Phys Chem B* 110(48):24492–24497. <https://doi.org/10.1021/jp063506y>
2. Liu X, Dilger H, Eichel RA, Kunstmann J, Roduner EA (2006) Small Paramagnetic Platinum Cluster in an NaY Zeolite: Characterization and Hydrogen Adsorption and Desorption. *J Phys Chem B* 110(5):2013–2023. <https://doi.org/10.1021/jp0561874>
3. Frances L, Grivet M, Renault J-P, Groetz J-E, Ducret D (2015) Hydrogen Radiolytic Release from Zeolite 4A/Water Systems under γ Irradiations. *Radiat Phys Chem* 110:6–11. <https://doi.org/10.1016/j.radphyschem.2015.01.008>
4. Kumagai Y (2014) Decomposition of Hydrogen Peroxide by γ -Ray Irradiation in Mixture of Aqueous Solution and Y-Type Zeolite. *Radiat Phys Chem* 97:223–232. <https://doi.org/10.1016/j.radphyschem.2013.12.006>
5. Le Caër S, Water Radiolysis (2011) Influence of Oxide Surfaces on H_2 Production under Ionizing Radiation. *Water* 3(1):235–253. <https://doi.org/10.3390/w3010235>
6. Ouerdane H, Gervais B, Zhou H, Beuve M, Renault J-P (2010) Radiolysis of Water Confined in Porous Silica: A Simulation Study of the Physicochemical Yields. *J Phys Chem C* 114(29):12667–12674. <https://doi.org/10.1021/jp103127j>
7. Chemerisov SD, Trifunac AD (2001) Probing Nanoconfined Water in Zeolite Cages: H Atom Dynamics and Spectroscopy. *Chem Phys Lett* 347(1–3):65–72. [https://doi.org/10.1016/S0009-2614\(01\)01009-0](https://doi.org/10.1016/S0009-2614(01)01009-0)
8. Frances L, Douilly M, Grivet M, Ducret D, Théobald M (2015) Self-Radiolysis of Tritiated Water Stored in Zeolites 4A: Production and Behavior of H_2 and O_2 . *J Phys Chem C* 119(51):28462–28469. <https://doi.org/10.1021/acs.jpcc.5b10243>
9. Foley S, Rotureau P, Pin S, Baldacchino G, Renault J-P, Mialocq J-C (2005) Radiolysis of Confined Water: Production and Reactivity of Hydroxyl Radicals. *Angew Chem Int Ed* 44(1):110–112. <https://doi.org/10.1002/anie.200460284>
10. Fourdrin C, Aarrachi H, Latrille C, Esnouf S, Bergaya F, Le Caër S (2013) Water Radiolysis in Exchanged-Montmorillonites: The H_2 Production Mechanisms. *Environ Sci Technol* 47(16):9530–

9537. <https://doi.org/10.1021/es401490t>

11. Brodie-Linder N, Le Caër S, Alam MS, Renault J-P, Alba-Simionesco C (2010) H₂ Formation by Electron Irradiation of SBA-15 Materials and the Effect of Cu(II) Grafting. *Phys Chem Chem Phys* 12(42):14188–14195. <https://doi.org/10.1039/C0CP00115E>
12. Kumagai Y, Kimura A, Taguchi M, Watanabe M (2017) Hydrogen Production by γ -Ray Irradiation from Different Types of Zeolites in Aqueous Solution. *J Phys Chem C* 121(34):18525–18533. <https://doi.org/10.1021/acs.jpcc.7b03532>
13. Hu C, Cheng L, Zhou L, Jiang Z, Gan P, Cao S, Li Q, Chen C, Wang Y, Mostafavi M, Wang S, Ma J (2023) Radiolytic Water Splitting Sensitized by Nanoscale Metal–Organic Frameworks. *J Am Chem Soc* 145(9):5578–5588. <https://doi.org/10.1021/jacs.3c00547>
14. McGrady J, Yamashita S, Kano S, Yang H, Kimura A, Taguchi M, Abe H (2023) Radiolysis of Water at the Surface of ZrO₂ Nanoparticles. *Radiat Phys Chem* 209:110970. <https://doi.org/10.1016/j.radphyschem.2023.110970>
15. Li L, Xu X, Ye M, Liu Z (2025) Toward Realistic Simulations of Zeolite Catalytic Processes: A Mini Review. *J Phys Chem C* 129(1):24–36. <https://doi.org/10.1021/acs.jpcc.4c07342>
16. Shin H, Choi M, Kim HA (2016) Mechanistic Model for Hydrogen Activation, Spillover, and Its Chemical Reaction in a Zeolite-Encapsulated Pt Catalyst. *Phys Chem Chem Phys* 18(10):7035–7041. <https://doi.org/10.1039/C5CP05536A>
17. Chemerisov SC, Werst DW, Trifunac AD, Formation (2001) Trapping and Kinetics of H Atoms in Wet Zeolites and Mesoporous Silica. *Radiat Phys Chem* 60(4–5):405–410. [https://doi.org/10.1016/S0969-806X\(00\)00408-4](https://doi.org/10.1016/S0969-806X(00)00408-4)
18. Spinks JWT, Woods RJ (1990) *An Introduction to Radiation Chemistry*, 3rd ed.; John Wiley & Sons: New York
19. Pimblott SM, LaVerne JA (2007) Production of Low-Energy Electrons by Ionizing Radiation. *Radiat Phys Chem* 76(8–9):1244–1247. <https://doi.org/10.1016/j.radphyschem.2007.02.012>
20. Cordischi D, Occhiuzzi M, Dragone R, Quantitative EPR, Spectroscopy (1999) Comparison between Primary Standards and Application to MgO–MnO and α -Al₂O₃–Cr₂O₃ Solid Solutions. *Appl Magn Reson* 16(3):427–445. <https://doi.org/10.1007/BF03161929>

Figures

EXPERIMENTAL PROCEDURE

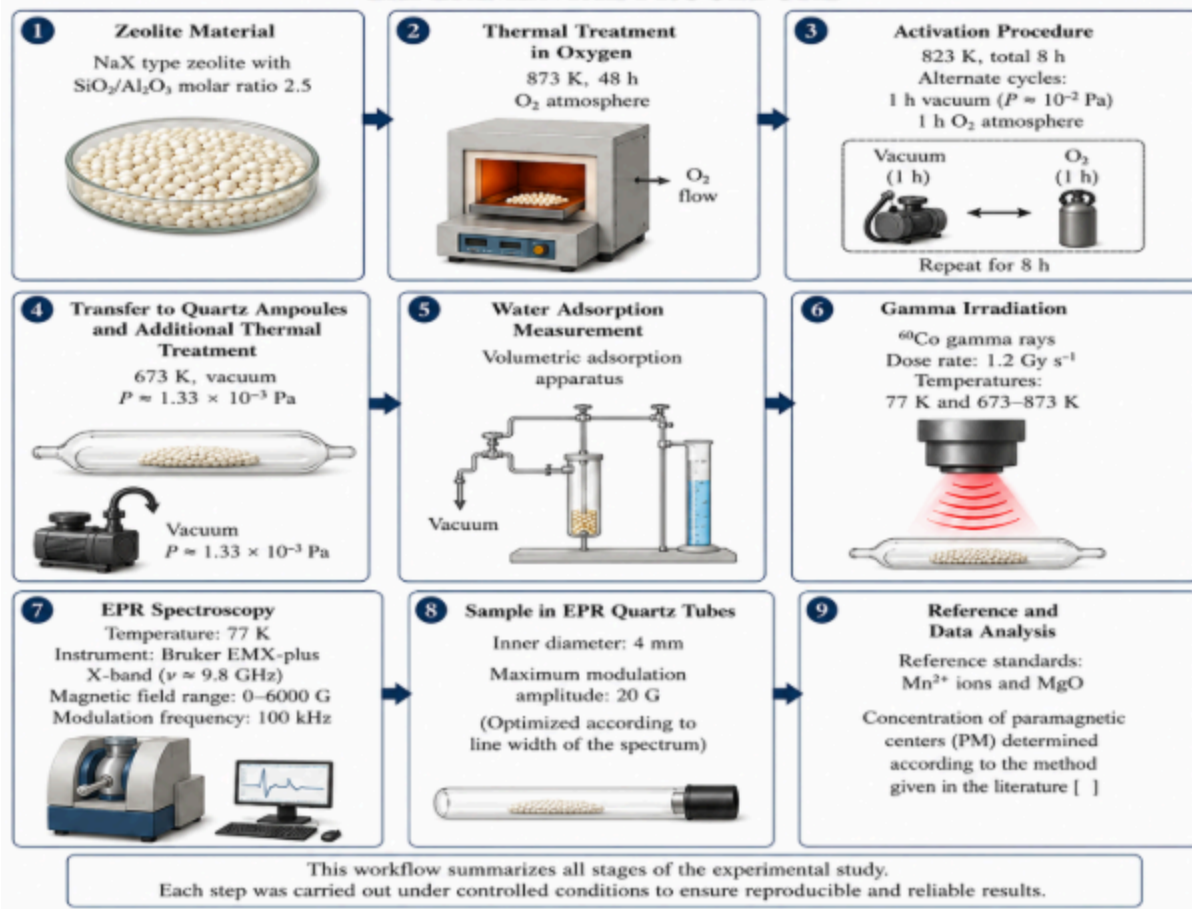


Figure 1

Schematic flow diagram of the experimental procedure.

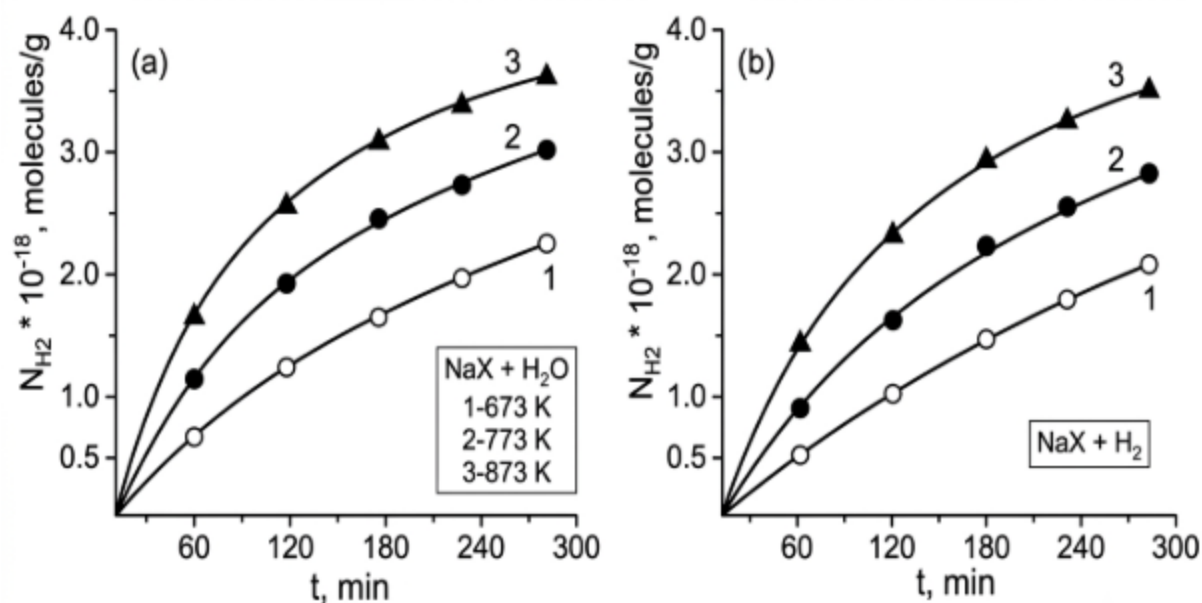


Figure 2

Kinetics of molecular hydrogen evolution during thermocatalytic (a) and radiation-assisted thermocatalytic (b) water decomposition in the presence of NaX zeolite. Curves correspond to temperatures of 673 K (1), 773 K (2), and 873 K (3).

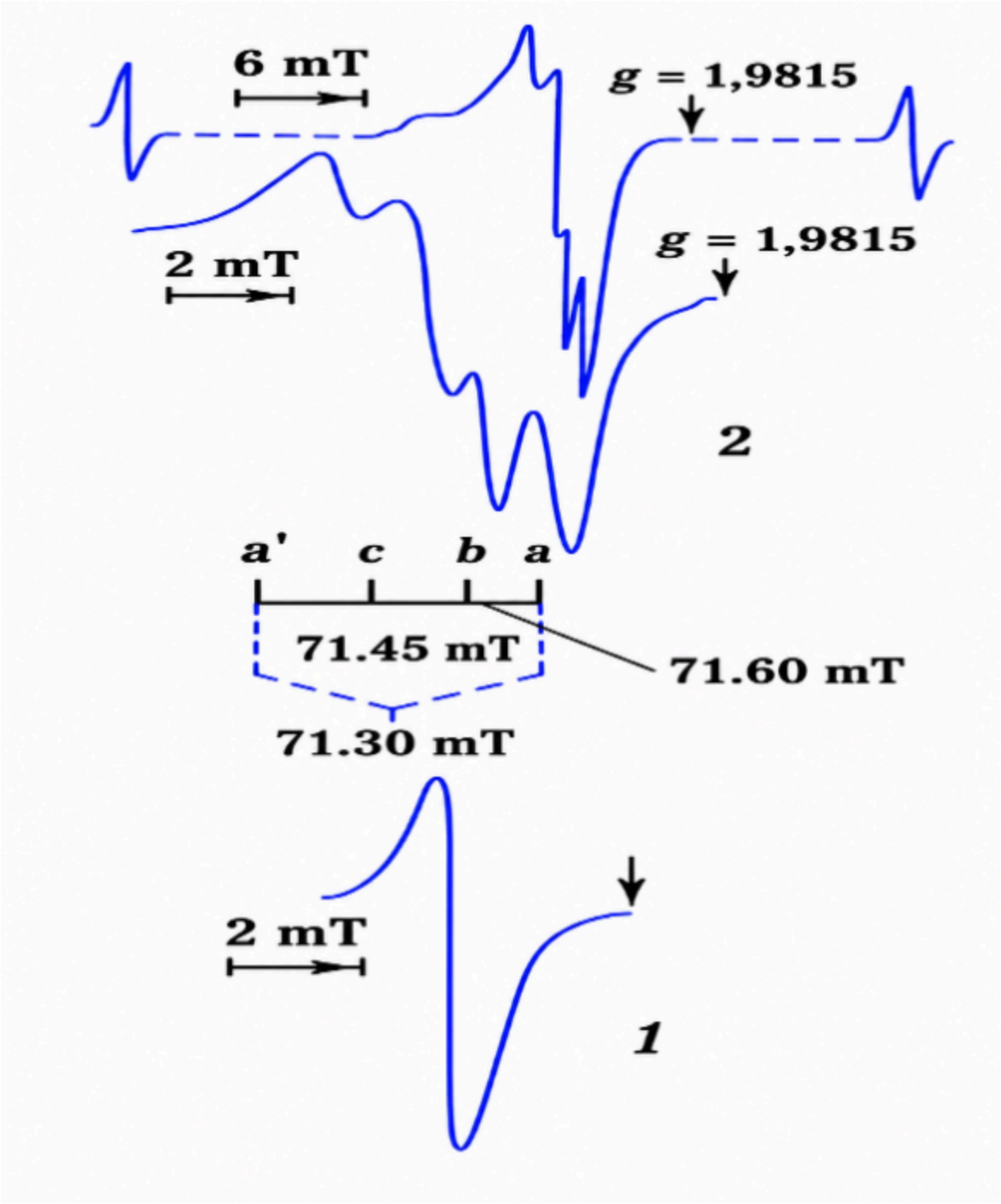


Figure 3

EPR spectra of the γ -irradiated NaX zeolite–H₂O system at water contents of $\mu\text{H}_2\text{O} = 1 \times 10^3 \mu\text{mol g}^{-1}$ (1) and $\mu\text{H}_2\text{O} > 1 \times 10^3 \mu\text{mol g}^{-1}$ (2).

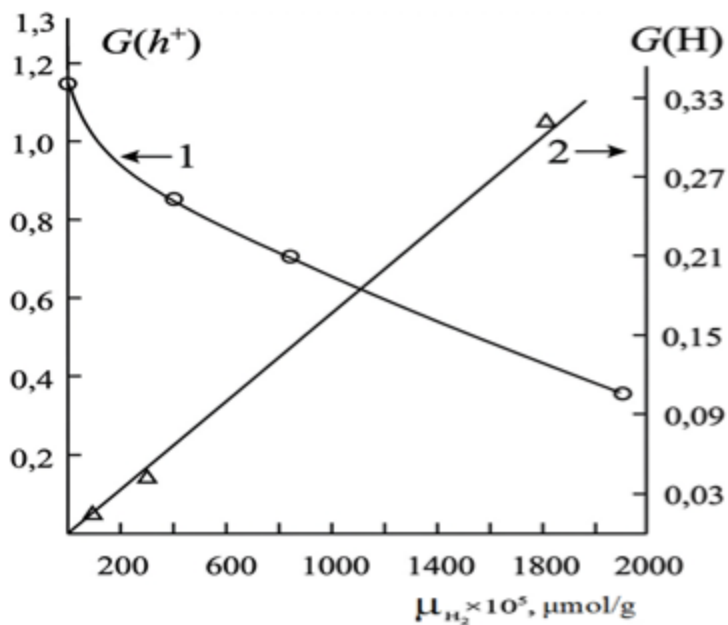


Figure 4

Dependence of the radiation-chemical yield of radiation-induced defects in the zeolite (1) and stabilized hydrogen atoms (2) on the amount of adsorbed water in the NaX zeolite-H₂O system under γ-irradiation at T = 77 K.

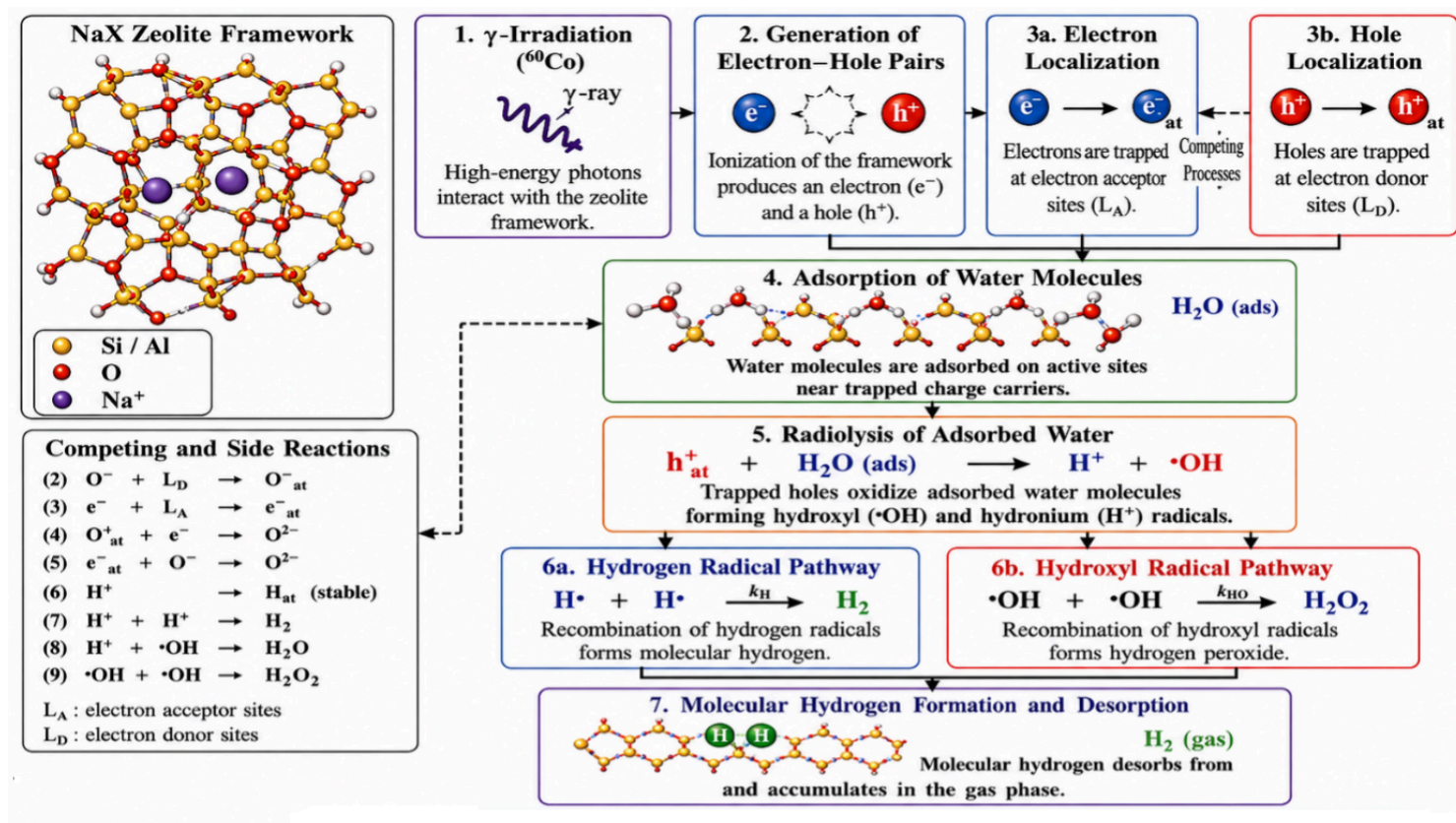


Figure 5

Proposed reaction mechanism for radiation-induced heterogeneous water splitting and hydrogen formation on NaX zeolite under γ -irradiation.