Photocatalytic generation of useful hydrocarbons and hydrogen from acetic acid in the presence of lanthanide modified TiO₂

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1. Introduction

Economic and industrial development is strongly dependent on accessibility of fossil fuels. Their high price, depletion of natural resources as well as environmental concerns have forced scientists to search for clean and renewable energy sources [1,2]. One of the most promising alternatives for fossil fuels seems to be biogas. It is considered an environmentally friendly, economic and energy efficient fuel [1,3].

Conventional biogas production is based on anaerobic digestion or fermentation of organic matter under anaerobic conditions. However, despite of the unchallenged qualities, this process can be affected by many factors such as the origin and concentration of organic matter, oxygen concentration and the pH value. In addition, bacteria are not able to treat substances which are biorecalcitrant (e.g. herbicides) or bactericide. This reduces the number of possible substrates to those which do not contain substances dangerous to the bacteria [4,5]. In response to that, the production of hydrocarbons and hydrogen from organic matter via photocatalytic reaction appears to be a very attractive alternative to the conventional biogas generation. Due to the fact that
photocatalysis is not specific (or almost not) for the particular substances it could be applied for any type of wastewaters, regardless of its toxicity [3].

Titanium dioxide (TiO₂) is one of the most often applied photocatalysts due to its high activity, low costs and excellent resistance to chemical and photochemical corrosion in aggressive aqueous environments [6]. Nevertheless, there are several limitations which have to be considered when using TiO₂, e.g. its high energy band gap, recombination of photo-induced electron/hole pairs and low interfacial charge transfer. Modification of TiO₂ with different metals is one of methods to overcome the above problems.

Modification of TiO₂ with lanthanides has been widely investigated and presented in numerous publications as an effective method of enhancement of activity of the photocatalysts towards both air and aqueous solutions purification. It is well known that, the lanthanide ions have a strong ability to form complexes with various Lewis bases, such as acids, aldehydes and alcohols, through the interaction of their functional groups with the f-orbital of the lanthanides. This leads to increase the adsorption capacity of Ln modified TiO₂ [7–9]. Moreover, lanthanides can retard the transformation from anatase to rutile and brookite phases (regarded as less active ones) and also decrease the electron—hole recombination rate [10].

Literature data describing photocatalytic generation of useful hydrocarbons from organic compounds in the liquid phase over TiO₂ are very limited [11–15]. First research results concerning photocatalytic degradation of acetic acid over Pt/TiO₂ were published over thirty years ago by Kraeutler and Bard [11–13]. During the so-called “photo-Kolbe” reaction CH₃COOH undergoes decarboxylation and as a result CH₄ and CO₂ are formed. Unfortunately, no significant progress in this area was accomplished since then. All the more, no attempts of using Ln³⁺/TiO₂ in a photocatalytic generation of useful hydrocarbons can be found among literature data.

Taking above into consideration, in the present study we have focused on preparation of samarium and europium modified TiO₂ photocatalysts and their application for generation of useful hydrocarbons (mainly CH₄) and H₂ from CH₃COOH under N₂ atmosphere. Acetic acid was used as a model compound due to the fact that among many by-products of degradation of organic compounds different aliphatic acids, including CH₃COOH, are present. Moreover, it seems reasonable to use this compound since it was proved that it is possible to produce CH₄ from CH₃COOH in a photo-Kolbe reaction.

2. Experimental

2.1. Preparation of the photocatalysts

Lanthanide (Eu³⁺ or Sm³⁺) modified TiO₂ photocatalysts were prepared by a sol–gel method. Titanium(IV)isopropoxide (TTIP, Ti(OiC₃H₇)₄, Fluka) solution was added dropwise under vigorous stirring into aqueous solution of nitric acid (pH = 2). Then proper amount of either europium or samarium nitrate (Eu(NO₃)₃ and Sm(NO₃)₃, 99.9%, Aldrich) were added to the above mixture which was stirred for 24 h at 70–80 °C. The semi-transparent colloidal suspension solution was evaporated at 70–80 °C until the formation of powder. The powder was then grounded and heat treated at 450 °C for 2 h. The amounts of Eu and Sm introduced into the samples were 0.007, 0.02, 0.05 and 0.07 mol%. Analogously, pure TiO₂ without addition of lanthanides ions precursors was prepared in order to compare the results. Moreover, commercially available photocatalyst AEOROXIDE® P25 (Evonik, Germany) was also applied during a photocatalytic reaction. The P25 photocatalyst was composed of anatase (82%) and rutile (18%). The specific BET surface area of P25 was 50 m²/g and the average anatase crystallite size was 22 nm.

2.2. Characterization of the photocatalysts

The XRD patterns were recorded using PHILIPS diffractometer with CuKα radiation (k = 1.54056Å). The accelerating voltage of 40 kV and emission current of 30 mA were used.

The phase composition of the photocatalysts was calculated from:

\[ W_A = K_A A_A / [ K_A A_A + K_B A_B + A_S ] \]  
\[ W_B = K_B A_B / [ K_A A_A + K_B A_B + A_S ] \]

where \( W_A \) and \( W_B \) represent the weight of the anatase and brookite phases, respectively; \( A_A, A_B \) and \( A_S \) - the diffraction intensities of the anatase (101) brookite (121) and rutile (110) crystalline phases, respectively; the variables \( K_A \) and \( K_B \) are coefficients with values 0.886 and 2.721, respectively [16–18]. The average anatase crystallite diameter \( L \) (nm) was calculated using Scherrer’s equation [19,20]:

\[ L = K \lambda / \beta \cos \theta \]

where \( K = 0.9 \) is a shape factor for spherical particles, \( \lambda \) is the wavelength of the incident radiation (\( \lambda = 1.54056 \AA \)), \( \beta \) is half of the diffraction angle (rad) and \( \beta \) is the line width at half-maximum height.

The UV–vis/DR spectra were recorded using Jasco V530 spectrometer (Japan) equipped with an integrating sphere accessory for diffuse reflectance spectra. BaSO₄ was used as a reference.

The FTIR spectra were recorded using Jasco FT-IR 430 spectrometer (Japan) equipped with a diffuse reflectance accessory (Harrick, USA).

XPS studies have been carried out with use of PREVAC electron spectrometer, equipped with SES 2002 (VG Scienta) electron energy analyzer. Samples were excited with use of dual anode (Mg/Al) x-ray source. Eu³⁺ doped and pure TiO₂ sample were excited by Al Kα radiation, while Sm³⁺ doped sample by Mg Kα. The binding energies were referenced to carbon C 1s peak at 284.6 eV (adventitious carbon). Quantitative analysis of the surface composition was based on the homogenous model and calculated in CasaXPS.

The Brunauer–Emmett–Teller (BET) surface area of the powders was determined on the basis of nitrogen adsorption–desorption measurements at 77 K. The BET surface area \( S_{BET} \) was determined by multipoint BET method using the
adsorption data. The total pore volume ($V_p$) ($\text{cm}^3 \text{ g}^{-1}$) was derived from the amount of vapor adsorbed at a relative pressure close to unity by assuming that the pores are filled with liquid adsorbate:

$$V_p = V (P/P^0 = 1) \times 0.001554$$

where: $P$ is the measured equilibrium pressure, $P^0$ is the saturated vapor pressure of the adsorbate at the temperature of the experiment, $V$ is the amount of gas adsorbed in cm$^3$ per gram of adsorbent.

Assuming that pores are cylindrical the average pore size $r_p$ was calculated as follows:

$$r_p = 4 V_p \times 10^9/S_{BET}$$

2.3. Photocatalytic reaction

The photocatalytic reaction was carried in a cylindrical glass reactor containing 0.35 dm$^3$ of CH$_3$COOH (1 mol/dm$^3$) and 0.35 g of a catalyst. At the beginning of the experiment N$_2$ was bubbled through the reactor for at least 1 h to remove all of the dissolved oxygen. Then, the UV lamp ($\lambda_{max} = 365$ nm), positioned in the center of the reactor was turned on to start the photoreaction. The process was conducted for 27 h. All the experiments were repeated at least twice in order to confirm the reproducibility of the results. The presented data are mean values obtained from the two experiments.

Gaseous products of the reaction were analyzed using GC SRI 8610C equipped with TCD and FID detectors, and Shimadzu (carbon molecular sieve; 2 m, 1 mm, 100–120 mesh) and molecular sieve 5 A (3 m, 2 mm, 80–100 mesh) columns. Helium was used as the carrier gas. The composition of the liquid phase was determined using GC SRI 8610C equipped with FID detector and MXT$^{\text{TM}}$ – 1301 (60 m) column. Hydrogen was used as the carrier gas.

3. Results and discussion

3.1. Physico–chemical properties of the photocatalysts

Fig. 1 shows the XRD patterns of the pure TiO$_2$, 0.07 mol% Eu$^{3+}$/TiO$_2$ and 0.07 mol% Sm$^{3+}$/TiO$_2$. The phase composition of the photocatalysts is presented in Table 1. Pure TiO$_2$ contained anatase ($20 = 25.68^\circ$) and brookite ($20 = 31.10^\circ$) phases in the ratio of 60.3:30.7, whereas Sm and Eu modified samples existed as a single anatase phase. The crystallite size of anatase in the pure TiO$_2$ was 10 nm. In case of the samples modified with Sm and Eu ions the crystallite size of anatase was in the range of 6–10 nm (Table 1). It is well known that Sm$^{3+}$ or Eu$^{3+}$ rather unlikely cooperate with the matrix of TiO$_2$ because of the mismatch of the ionic radii of Ti$^{4+}$ and lanthanide ions. Literature data indicate that the surrounding lanthanide ions can inhibit the phase transition through the formation of Ti–O–Ln bond. Furthermore, the Ln lattice can lock the Ti–O species at the interface with TiO$_2$ domains and prevent the nucleation necessary for the transformation of anatase to rutile or brookite phases, which results in the decrease of the crystallite size of the photocatalysts [21,22].

The specific surface area ($S_{BET}$), the pore volume ($V_p$) and pore diameter ($r_p$) of the photocatalysts are presented in Table 1. It can be seen that the surface area of the titania increased as a result of introduction of lanthanide ions from 154 m$^2$/g in case of pure TiO$_2$ to 182–201 m$^2$/g for Sm/TiO$_2$ and 171–198 for Eu/TiO$_2$. These results confirm the conclusions drawn on a basis of the XRD measurements that the addition of lanthanides can effectively inhibit the sintering of nanoparticles and suppress the growth of TiO$_2$ crystallites [21,23–28].

The average pore size of the prepared photocatalysts ranged from 5.2 to 7.4 nm, which confirms the formation of mesoporous structures. Moreover, the average pore volume was slightly higher in case of Ln$^{3+}$/doped TiO$_2$ compared to pure titania.

UV–vis/DR spectra (Fig. 2) of the pure TiO$_2$ as well as the Sm and Eu modified powders (0.007 mol% and 0.07 mol% La$^{3+}$/TiO$_2$ were selected as examples) indicate that the light absorption characteristics of the photocatalysts were affected by the presence of lanthanides ions. In the spectra of the 0.07 mol % Sm$^{3+}$/TiO$_2$ and Eu$^{3+}$/TiO$_2$ photocatalysts distinct absorption bands in the wavelength range of about 400–670 nm are present. The main bands are located at 404, 463, 477, 527, 562 nm in case of Sm$^{3+}$/TiO$_2$ and at 456, 526, 533, 578 nm in case of Eu$^{3+}$/TiO$_2$. The occurrence of these bands indicates that the lanthanide doped samples might be in favor of visible – light absorption [21]. According to Liang et al. [23] the transitions of electrons between energy levels have to be taken into consideration in case of lanthanide modified photocatalysts. This kind of transitions could be responsible for good separation of photogenerated electron – hole pairs. Moreover, since lanthanide ions posses a broad absorption band in visible region their incorporation into TiO$_2$ structure can cause a photosensitizing effect. The Sm or Eu ions can surround the titania grains and absorb a large range of light radiation. This behavior might be responsible for the “waving” observed in the presented spectra [21]. The lack of the above discussed absorption bands in case of 0.007 mol% Sm$^{3+}$/TiO$_2$ and Eu$^{3+}$/TiO$_2$ samples were probably due to very low concentration of lanthanides ions incorporated in the catalysts structure.

Fig. 3 shows the FTIR spectra of the pure TiO$_2$, commercially available P25 as well as the lanthanides (0.007 mol% and 0.07 mol% Sm and Eu) modified powders. In the region of 3300–3500 cm$^{-1}$ the bands associated with –OH vibrations could be seen. The bands observed at 1630–1640 cm$^{-1}$ can be assigned to the molecular water bending mode [29]. All spectra exhibited in the (–OH) region one band with
a maximum at 3665–3700 cm\(^{-1}\), which characterizes the stretching vibrations of Ti\(^{4+}\)–OH surface hydroxyl groups. In the low frequency region (below 1000 cm\(^{-1}\)) the self-absorption of titania \([30]\) was observed. Moreover, in case of Eu and Sm modified photocatalysts the bands at 1300–1580 and 1370–1505 cm\(^{-1}\) were observed, respectively. After comparison of the spectrum of the sample containing 0.07 mol% of Sm with the spectrum of samarium oxide, it was found that these absorption bands could be assigned to the stretching vibrations of Sm–O–Sm in Sm\(_2\)O\(_3\). Similarly, the bands at 1300–1580 cm\(^{-1}\) in case of Eu modified TiO\(_2\) were attributed to europium oxide.

XPS analyses of pure TiO\(_2\), as well as Eu- and Sm-doped TiO\(_2\) samples containing 0.07 mol% of Ln were carried out to determine the valence states of various species present in the composite. All elements detected on the surface of studied samples by XPS analysis and their surface concentrations are collected in Table 2. Carbon present in all samples is considered to be a contamination coming from preparation stages or adsorbed during experiments under vacuum. Surface concentration of europium and samarium atoms substantially exceeds the total concentration of that elements in the samples (0.07 mol%). It indicates that the preparation procedure leads to the enrichment of the crystallite’s surface with dopants. Even the calcination of the samples at elevated temperature didn’t give a homogenous distribution of Ln atoms in the product. Since dopants oxides seem to be present on the surface of the TiO ratio does not reflect the bulk TiO\(_2\) stoichiometry and cannot be taken as a measure of TiO\(_2\) defects.

Fig. 4(a–d) show high resolution XP spectra of Ti 2p, Ti O1s, Eu 3d and Sm 3d of pure TiO\(_2\) and TiO\(_2\) containing 0.07 mol% of dopants. The XPS Ti 2p spectrum of the pure TiO\(_2\) shows the two peaks at 458.6 eV and 464.3 eV, which were assigned to Ti 2p\(_{3/2}\) and Ti 2p\(_{1/2}\), respectively, indicating that the titanium exists in the chemical state of Ti\(^{4+}\) \([27,28]\). There is a very small peak shift of Ti 2p peak maximum toward low binding energy observed for doped samples. Similar shift was previously attributed to the change of the local chemical environment of Ti ions influenced by Ln incorporation and to the formation of Eu–O–Ti bonds on the surface of TiO\(_2\) \([31,32]\).

The XPS O 1s are relatively broad (FWHM about 2.0 eV) and asymmetric indicating the existence of more than one
chemical state convoluted in these spectra. These spectra were fitted with the nonlinear least-squares fit program using Gauss–Lorentzian peak shapes, assuming only two O1s peak components (see Fig. 4b). These two oxygen species are assigned to lattice oxygen (OTi–O or OLn–O at 529.9 eV) and the chemisorbed surface hydroxyl oxygen (OO–H at 531.4 eV), respectively [33,34]. The shift of O 1s binding energy for the Ln3+/TiO2 photocatalysts as compared to the O 1s state of the TiO2 films is similar to that observed for the Ti 2p state (Fig. 4b and Table 2).

The XPS Eu 3d spectrum for 0.07 Eu/TiO2 photocatalyst contains four distinct peaks. The peaks located at binding energies of 1135.2 eV and 1163.1 eV are assigned to Eu3+ ions. The other peaks at 1125.5 eV and 1152.4 eV are attributed to a Eu2+ oxidation state (Fig. 4c and Table 2) [35]. The appearance of Eu2+ ions is not expected after preparation stage; however, the photoreduction of Eu3+ to Eu2+ during the XPS measurements is a reasonable source of Eu2+ ions.

In Fig. 4d XPS Sm 3d spectrum is shown. There are two distinct peaks observed, at 1083.5 eV and 1110.0 eV. This doublet is assigned to Sm 3d5/2 and Sm 3d3/2 levels, respectively, coming from Sm3+ ions [36].

### Table 2 – The XPS data of the pure TiO2, 0.07% Sm3+/TiO2 and 0.07% Eu3+/TiO2 photocatalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Atomic %</th>
<th>Binding energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ti</td>
<td>O</td>
</tr>
<tr>
<td>Pure TiO2</td>
<td>22.2</td>
<td>65.7</td>
</tr>
<tr>
<td>0.07 mol% Eu3+/TiO2</td>
<td>20.0</td>
<td>65.1</td>
</tr>
<tr>
<td>0.07 mol% Sm3+/TiO2</td>
<td>20.3</td>
<td>60.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti 2p3/2</td>
<td>458.6</td>
<td>464.3</td>
</tr>
<tr>
<td>Ti 2p1/2</td>
<td>458.8</td>
<td>464.0</td>
</tr>
<tr>
<td>O1sL</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O1sS</td>
<td>1125.5, 1152.4</td>
<td>1135.2, 1163.1</td>
</tr>
<tr>
<td>Sm 3d</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eu3d</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.2. Photocatalytic decomposition of acetic acid

Pure and lanthanide modified TiO2 photocatalysts as well as the commercially available P25 were applied in the photocatalytic decomposition of acetic acid under N2 atmosphere. The reaction was conducted for 27 h. Regardless of the photocatalyst used the main gaseous products identified during the photocatalytic decomposition of CH3COOH were CH4 and CO2. Moreover, C2H6 and H2 as well as very low concentrations of C3H8 were present in the reaction mixture. The concentrations of these compounds in the gaseous phase (headspace volume of the reactor) were dependent on the photocatalyst applied and increased in time of irradiation.

3.2.1. Hydrocarbons production from acetic acid

The main objective of the present study was to investigate the photocatalytic generation of hydrocarbons, mainly methane, in the presence of different photocatalyst. The obtained results are presented in Fig. 5 and in Table 3. Methane and carbon dioxide formation during photocatalytic decomposition of acetic acid follows the so called photo-Kolbe reaction pathway [11–13,15]:

![Fig. 4 – High-resolution XPS of a) Ti 2p b) Ti O1s c) Eu 3d and d) Sm 3d of pure TiO2, 0.07% doped TiO2 photocatalysts.](image-url)
The reaction of the formation of ethane from acetic acid can be written as follows \([15]\):

\[
2 \text{CH}_3\text{COOH} \rightarrow \text{C}_2\text{H}_6 + 2 \text{CO}_2 + \text{H}_2 \quad \text{(7)}
\]

or, taking into consideration the recombination of methyl radicals \([37]\):

\[
\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6 \quad \text{(8)}
\]

Fig. 5 illustrates the influence of Eu\(^{3+}\) and Sm\(^{3+}\) ions concentration on the evolution rate of CH\(_4\) from CH\(_3\)COOH under UV light illumination. In general, the Sm modified samples exhibited higher activity towards methane generation than the Eu modified ones. After 27 h of irradiation the amount of CH\(_4\) was in the range of 1.26–3.34 mmol/mol CH\(_3\)COOH (Table 3). The highest yield of methane evolution was observed for 0.05 mol\%/Sm\(^{3+}\)/TiO\(_2\) and the lowest one for 0.02 mol\%/Sm\(^{3+}\)/TiO\(_2\). Methane evolution in case of commercial P25 was very low and comparable to that obtained in case of the least active 0.02 mol\%/Sm\(^{3+}\)/TiO\(_2\) (1.37 vs. 1.26 mmol/mol CH\(_3\)COOH, respectively).

The amount of CO\(_2\) at the end of the process ranged from 1.12 to 3.54 mmol/mol CH\(_3\)COOH (Table 3). The lowest concentration of CO\(_2\) was observed in case of 0.02 mol\%/Sm\(^{3+}\)/TiO\(_2\), whereas the highest was found in case of 0.05 mol\%/Sm\(^{3+}\)/TiO\(_2\) photocatalysts.

Amongst the gaseous products of the reaction ethane was also identified. The amount of C\(_2\)H\(_6\) evolved in the presence of different photocatalysts is shown in Table 3. In general, the amount of ethane was significantly lower compared to that of CH\(_4\) and CO\(_2\) which clearly indicates that the reaction in Eq. (7) was of minor importance. The amount of C\(_2\)H\(_6\) at the end of the irradiation was in the range of 0.050–0.116 mmol/mol CH\(_3\)COOH. The highest yield of ethane evolution was observed for P25 photocatalyst, whereas the lowest one for 0.05 mol\%/Eu\(^{3+}\)/TiO\(_2\).

Assuming that the main reaction pathway is the photo-Kolbe reaction (Eq. (6)), then every 1 mol of acetic acids should give 1 mol of methane and 1 mol of carbon dioxide, i.e. the CH\(_4\)/CO\(_2\) ratio should be equal to 1. In case of the prepared catalysts (pure and lanthanides modified TiO\(_2\)) the ratio was close to unity. However, in case of commercial P25 the CH\(_4\)/CO\(_2\) ratio was significantly lower and amounted to 0.65 (Table 3). This might suggest that except from the photo-Kolbe reaction (Eq. (6)) some other reactions in which CO\(_2\) is produced occurred in the presenting system. On a basis of the literature data \([15,38,39]\) as well as analysis of the results

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>mmol of CH(_3)COOH/mol CH(_4)/CO(_2)/C(_2)H(_6)/H(_2)</th>
<th>CH(_4)</th>
<th>CO(_2)</th>
<th>C(_2)H(_6)</th>
<th>H(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P25</td>
<td>1.49</td>
<td>1.37</td>
<td>2.08</td>
<td>0.116</td>
<td>0.065</td>
</tr>
<tr>
<td>Pure TiO(_2)</td>
<td>2.51</td>
<td>2.51</td>
<td>2.25</td>
<td>0.102</td>
<td>0.032</td>
</tr>
<tr>
<td>Eu/TiO(_2)</td>
<td>0.007%</td>
<td>2.62</td>
<td>2.40</td>
<td>0.064</td>
<td>0.096</td>
</tr>
<tr>
<td>Sm/TiO(_2)</td>
<td>0.007%</td>
<td>1.42</td>
<td>1.55</td>
<td>0.060</td>
<td>0.060</td>
</tr>
<tr>
<td>0.02%</td>
<td>2.91</td>
<td>2.91</td>
<td>2.38</td>
<td>0.110</td>
<td>0.230</td>
</tr>
<tr>
<td>0.05%</td>
<td>2.19</td>
<td>2.19</td>
<td>2.31</td>
<td>0.050</td>
<td>0.440</td>
</tr>
<tr>
<td>0.07%</td>
<td>1.49</td>
<td>1.49</td>
<td>1.83</td>
<td>0.110</td>
<td>0.198</td>
</tr>
<tr>
<td>0.007%</td>
<td>1.42</td>
<td>1.42</td>
<td>1.77</td>
<td>0.060</td>
<td>0.060</td>
</tr>
<tr>
<td>0.02%</td>
<td>1.26</td>
<td>1.26</td>
<td>1.12</td>
<td>0.070</td>
<td>0.090</td>
</tr>
<tr>
<td>0.05%</td>
<td>3.34</td>
<td>3.34</td>
<td>3.54</td>
<td>0.084</td>
<td>0.087</td>
</tr>
<tr>
<td>0.07%</td>
<td>2.59</td>
<td>2.59</td>
<td>2.29</td>
<td>0.111</td>
<td>0.092</td>
</tr>
</tbody>
</table>

Table 3 - The amount of gases evolved after 27 h of photocatalytic decomposition of acetic acid, CH\(_3\)/CO\(_2\)/C\(_2\)H\(_6\)/H\(_2\) ratio over various TiO\(_2\) catalysts.
obtained in our system, we propose that an excess of carbon
dioxide originated from mineralization of acetic acid to H2O
and CO2 [38]:

CH3COOH + 2O2 → 2CO2 + 2H2O  \hspace{1cm} (9)

P25 is well known from its high activity in degradation and
mineralization of organic compounds, which is associated
mainly with efficient formation of hydroxyl radicals. The
photo-Kolbe reaction mechanism is based on direct oxidation
of acetic acid molecules by h+ (Eq. [6]). Thus, the reaction
pathways based on oxidation by hydroxyl radicals are not
desirable for efficient formation of methane from acetic acid.
However, since no atmospheric O2 was present in the system,
the involvement of photogenerated oxygen should be
considered [40,41].

In order to clarify the reaction mechanism the composition of
the liquid phase was also determined. Amongst the by-
products of acetic acid decomposition methanol (CH3(OH)),
ethanol (CH3CH2OH), acetone (CO(CH3)3), acetaldehyde (CH2CHO)
and isopropanol ((CH3)2CHOH) were identified. The concen-
trations of these products were very low and did not exceed
0.08 μmol/dm3. The presence of the above mentioned reaction
products in liquid phase could be explained by assuming the
involvement of hydroxyl radicals [15].

On a basis of the results obtained at the end of irradiation
the activity of the photocatalysts towards methane generation
can be put in the following order: 0.05 mol% Sm3+/TiO2 >
0.02 mol% Eu3+/TiO2 > 0.007 mol% Eu3+/TiO2 = 0.07 mol
% Sm3+/TiO2 ≈ pure TiO2 > 0.05 mol% Eu3+/TiO2 > 0.07 mol%
Eu3+/TiO2 ≈ 0.007 mol% Sm3+/TiO2 ≈ P25 > 0.02 mol% Sm3+/TiO2.
Comparing these data with the specific BET surface area
(SBET) related to small crystallites size of anatase and the
presence of lanthanides ions determined the effectiveness of
the photocatalysts. Moreover, the obtained data revealed that
higher effectiveness of methane formation could be obtained
in case of Sm modified TiO2 than in case of Eu/TiO2.

Therefore, it seems that there is no one crucial factor
affecting photocatalytic activity of the samples. Both, high
SBET related to small crystallites size of anatase and the
presence of lanthanides ions determined the effectiveness of
the photocatalysts. Moreover, the obtained data revealed that
higher effectiveness of methane formation could be obtained
in case of Sm modified TiO2 than in case of Eu/TiO2.

3.2.2. Hydrogen production from acetic acid

As was mentioned above, hydrogen was also detected among
other gaseous products of the process (Table 3). There are
numerous publications concerning photocatalytic hydrogen
evolution in the presence of sacrificial agents, such as meth-
anol, ethanol, formic and acetic acids and acetaldehyde
[15,41,44–46]. In general, when a reducing agent, or hole
scavenger is present in the solution, photocatalysts is
enriched with electrons and H2 evolution reaction is enhanced:

2H+ + 2e− → H2  \hspace{1cm} (10)

Table 3 presents the amount of H2 in the gaseous phase
after 27 h of irradiation. It can be clearly seen that photo-
catalysts modified with Eu ions revealed higher effectiveness
of H2 generation compared to pure and commercially avail-
able TiO2 as well as the Sm3+/TiO2. As we remember, the
effectiveness of methane evolution was higher in case of
Sm3+/TiO2 than in case of Eu3+/TiO2. The highest yield of
hydrogen evolution was observed for TiO2 containing 0.05 mol%
of Eu (0.44 mmol/mol CH3COOH). Apparently, high photo-
activity of this sample toward H2 production was associated
with the presence of Eu. No significant improvements of the
effectiveness of H2 production compared to pure TiO2 and P25
could be observed in case of samarium modified samples. It is
well known that the lanthanide ions bonded on the surface
of TiO2 particles act as good scavengers of the photoelectrons
[21,42,43]. The electronic structure of lanthanide ions can
form new energy states inside the band gap of TiO2. It was also
reported that Sm and Eu ions form a shallow impurity states
(electron transfer from valence band to lanthanide energy
state) inside the conduction and valence bands [47,48]. Doping
of TiO₂ with lanthanide metal ions results in retardation of the recombination rate of the electron — hole pairs by means of scavenging of the excited electrons from TiO₂ valence band to form Ln²⁺. However, the most stable oxidation state of lanthanides is +3. Thus, the electrons are subsequently transferred from the reduced lanthanide ion to the proton to form hydrogen. It was also proved that Eu ions have very strong electron - trapping capacity, even stronger than other lanthanides elements [43]. It could be supposed that this was the main reason responsible for high photoactivity of Eu modified TiO₂ in case of hydrogen production from acetic acid. The obtained results clearly show that evolution of hydrogen was significantly lower than that of methane or carbon dioxide, even in case of Eu/TiO₂. The reason for that could be acidic pH of the reaction environment. It was reported that the H₂ production is favored in neutral or basic solutions [41].

4. Conclusions

Ln³⁺/TiO₂ photocatalysts with different Sm³⁺ or Eu³⁺ concentrations were prepared by a sol–gel method. All Ln³⁺/TiO₂ samples exhibited anatase crystalline phase and surface areas higher than the unmodified TiO₂.

Amongst the gaseous products identified during the photocatalytic decomposition of CH₄COOH the CH₄ and CO₂ were obtained at the highest amounts.

The most active photocatalyst toward CH₄ production was TiO₂ containing 0.05 mol% of Sm. The 0.05 mol% Sm³⁺/TiO₂ contained anatase (100%) with crystallite size equal to 6 nm. The high photocatalytic activity of this sample towards methane evolution was attributed to its high specific surface area, phase composition, crystallite size of anatase and improved separation of the photogenerated electron — holes pairs due to the presence of Sm.

On the opposite, it was found that H₂ production was the most effective in case of TiO₂ modified with Eu. Since Eu ions can act as a strong electron scavengers their incorporation into the TiO₂ lattice was the most probably reason for the high activity of these photocatalysts.

REFERENCES


