

Research Article

Generation of Useful Hydrocarbons and Hydrogen during Photocatalytic Decomposition of Acetic Acid on CuO/Rutile Photocatalysts

Sylvia Mozia

Institute of Chemical and Environment Engineering, West Pomeranian University of Technology, ul. Pułaskiego 10, 70-322 Szczecin, Poland

Correspondence should be addressed to Sylvia Mozia, sylwiam@ps.pl

Received 14 May 2009; Accepted 14 May 2009

Recommended by Mohamed Sabry Abdel-Mottaleb

The presented studies have focused on a photocatalytic generation of useful hydrocarbons, mainly methane and ethane, from acetic acid under N_2 atmosphere. CuO-loaded rutile, as well as unmodified rutile and anatase-phase TiO_2 photocatalysts were applied in the experiments. The efficiency of the catalysts towards methane generation changed in the following order: Cu- TiO_2 (10% Cu) > crude TiO_2 \approx Cu- TiO_2 (20% Cu) > Cu- TiO_2 (5% Cu) > rutile. The amount of CH_4 produced in the presence of the catalyst containing 10 wt% of Cu was higher for ca. 33% than in case of pure rutile. The concentration of ethane was 14–16 times lower than the amount of methane, regardless of the catalyst used. Low concentrations of hydrogen were also detected in the gaseous mixtures. After 5 hours of the process conducted with the catalyst containing 5–20 wt% of Cu the concentration of hydrogen amounted to 0.06–0.14 vol.%, respectively.

Copyright © 2009 Sylvia Mozia. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

1. Introduction

Energy has progressively become a major global concern due to the depletion of natural resources and the global warming problem. Moreover, although the oil prices, compared to the prices in summer last year, have recently decreased due to the global recession, it is impossible to predict what oil prices will be next year. In view of this, the development of renewable energy sources is very important. Among numerous alternative energy sources, bioenergy, especially biogas, seems to be the most environmentally friendly and economically viable one. Moreover, except from being the source of energy, the biogas could be an effective solution to the wastes and wastewaters problem.

Biogas typically refers to a mixture of gases, mainly methane and carbon dioxide, produced by the anaerobic digestion or fermentation of organic matter under anaerobic conditions. Other compounds present in the biogas could be N_2 , H_2 , H_2S , O_2 , CO , H_2O , and NH_3 . The composition of biogas varies depending on the origin of wastes used in the anaerobic digestion process as well as the process conditions.

The traditional production of biogas based on anaerobic digestion technology requires the presence of particular kinds of bacteria. The methanogenic bacteria are highly sensitive to the O_2 concentration in the system and their activities depend on the concentrations of fatty and acetic acids, and the pH value [1]. In addition, bacteria are not able to treat substances which are biorecalcitrant (e.g., herbicides) or bactericide. This reduces the number of possible sources for biogas generation to those which do not contain substances dangerous to the bacteria [2].

In view of this, it seems to be beneficial to find another solution for conversion of wastewaters into useful energy (biogas). In our opinion, such a solution could be development of biogas production via photocatalytic decomposition of organic compounds. Photocatalysis is not specific (or almost not) for particular substrates what means that could be applied for any type of wastewaters, regardless of its toxicity. Therefore, different biogas sources could be utilized for photocatalytic generation of biogas, or “photo-biogas”.

Most of the already published papers [3–11] on photocatalytic production of methane concern reduction of CO_2

under UV light in the presence of pure or modified TiO_2 . The reactions were carried out either in liquid or in gaseous phase. The efficient photoreduction of carbon dioxide in aqueous medium was found to be difficult since the solubility of carbon dioxide is rather low (ca. 0.03 mol/dm^3 at ambient conditions) [11]. Therefore, attempts to conduct the process in gaseous phase were made [12–14]. Generation of methane from CO_2 is often proposed as a method of solving the global warming problem. Another very important environmental problem is treatment of wastewaters. As was mentioned earlier, the photocatalytic production of methane from sewage is supposed to be helpful in solving this problem.

Literature data concerning photocatalytic generation of methane from organic compounds in liquid phase are very limited. All of them concern production of CH_4 from aliphatic acids [15–18] and alcohols [19]. In 1970's Kraeutler and Bard [15–17] published a series of papers concerning photocatalytic decarboxylation of acetic acid in the presence of Pt/TiO_2 catalyst. The main products of the reaction were methane and carbon dioxide. Similarly, Sakata et al. [18] observed formation of methane and ethane during photodecomposition of acetic and propionic acids in the presence of TiO_2 and Pt/TiO_2 .

One of the crucial points in the photocatalytic generation of methane from organic compounds is development of an effective photocatalyst. Most of literature data on the photocatalytic production of methane in aqueous phase show application of TiO_2 or Pt/TiO_2 photocatalysts [15–18]. In the presented studies we have focused on preparation of CuO -modified rutile photocatalysts and their application in photocatalytic generation of methane in N_2 atmosphere. CuO was selected on a basis of literature data [3, 20–23]. For example, Slamet et al. [3] found that CuO was very effective modifying agent in photoreduction of CO_2 . The authors investigated the effect of modification of TiO_2 with CuO , Cu_2O and Cu and found that CuO was the most active modifier compared to the other species. Sreethawong and Yoshikawa [23] reported that CuO/TiO_2 photocatalysts exhibited significant activity in photocatalytic hydrogen evolution. Taking into consideration these data, CuO was selected as a modifying agent in the presented experiments. Acetic acid was used as a source of the “photobiogas”. Application of acetic acid as a model compound seems to be reasonable since amongst the final by-products of photocatalytic degradation of most organic compounds in water different aliphatic acids, including CH_3COOH , are present.

2. Experimental

The catalysts used in this study were prepared from crude TiO_2 obtained directly from the Chemical Factory “Police” (Poland). The crude TiO_2 was modified with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ as follows. A defined amount of TiO_2 was introduced into a beaker containing aqueous solution of modifying agent and stirred for 22 hours. After that water was evaporated and the samples were dried at 105°C for 24 hours in an oven. Such prepared samples were calcinated at 700°C in Ar atmosphere ($5 \text{ dm}^3/\text{h}$) for 1 hour. The amount of Cu introduced to the

samples was 5, 10 or 20 wt%. In order to compare the results, a sample containing rutile phase without CuO was prepared by annealing of crude TiO_2 at 800°C for 1 hour in air. At the temperature of 700°C , which was applied for preparation of CuO /rutile catalysts, the anatase phase, not rutile, was obtained. Therefore, the temperature of 800°C was selected for preparation of pure rutile without CuO .

X-ray diffraction (XRD) analyses were performed on a powder diffractometer Philips X'Pert PRO ($\text{CuK}\alpha$, 35 kV, 30 mA). UV-VIS/DR spectra were recorded using Jasco V 530 spectrometer (Japan) equipped with the integrating sphere accessory for diffuse reflectance spectra. BaSO_4 was used as a reference.

The photocatalytic reaction was conducted in a cylindrical glass reactor containing 0.35 dm^3 of CH_3COOH (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 3 hours to ensure that the dissolved oxygen was eliminated. Then, the UV lamp ($\lambda_{\text{max}} = 365 \text{ nm}$), positioned in the center of the reactor, was turned on to start the photoreaction. Gaseous products were analyzed using GC SRI 8610C equipped with TCD and HID detectors, and Shincarbon (carbon molecular sieve; 4 m, 1 mm, 10–120 mesh) and molecular sieve 5A (2 m, 2 mm, 80–100 mesh) columns. Helium was used as a carrier gas.

3. Results and Discussion

Figure 1 presents XRD patterns of crude TiO_2 and photocatalysts modified with CuO . It can be observed that crude TiO_2 contained almost pure (97%) anatase phase. The diffraction lines were weak and broad suggesting poor crystallinity of the sample. The crystallite size of anatase in the crude TiO_2 was 9 nm. The catalysts containing 5 and 10 wt% Cu were composed of rutile and CuO only. In case of the sample containing 20 wt% of Cu , except from rutile and CuO phases, CuCl was also identified. The presence of CuCl suggests that the amount of CuCl_2 used was too high and the transformation of CuCl_2 to CuO was not complete under the conditions applied. Some amount of copper (II) was reduced to copper (I) forming CuCl . The sample prepared by calcination of crude TiO_2 at 800°C and denoted later as rutile consisted of 97% of rutile and 3% of anatase [24]. As was mentioned earlier (see Section 2), the temperature of 800°C was selected because application of calcination temperature of 700°C resulted not in rutile, but anatase phase. These data clearly show that the presence of CuO strongly affects the temperature of phase transformation from anatase to rutile. Such a phenomenon was already reported in literature [25]. Francisco and Mastelaro [25] explained it by catalyzing properties of copper oxide. CuO probably catalyzes the mass transport to the nucleation region of rutile phase, promoting rutile nuclei growth, thus favoring the phase transition. CuO is responsible for a higher number of defects inside the anatase phase, in such a way that formation and growth of a higher number of rutile nuclei into TiO_2 anatase take place faster. The mechanism responsible for such a modification is an excess of oxygen vacancies that accelerates the transition and the crystallite growth [25].

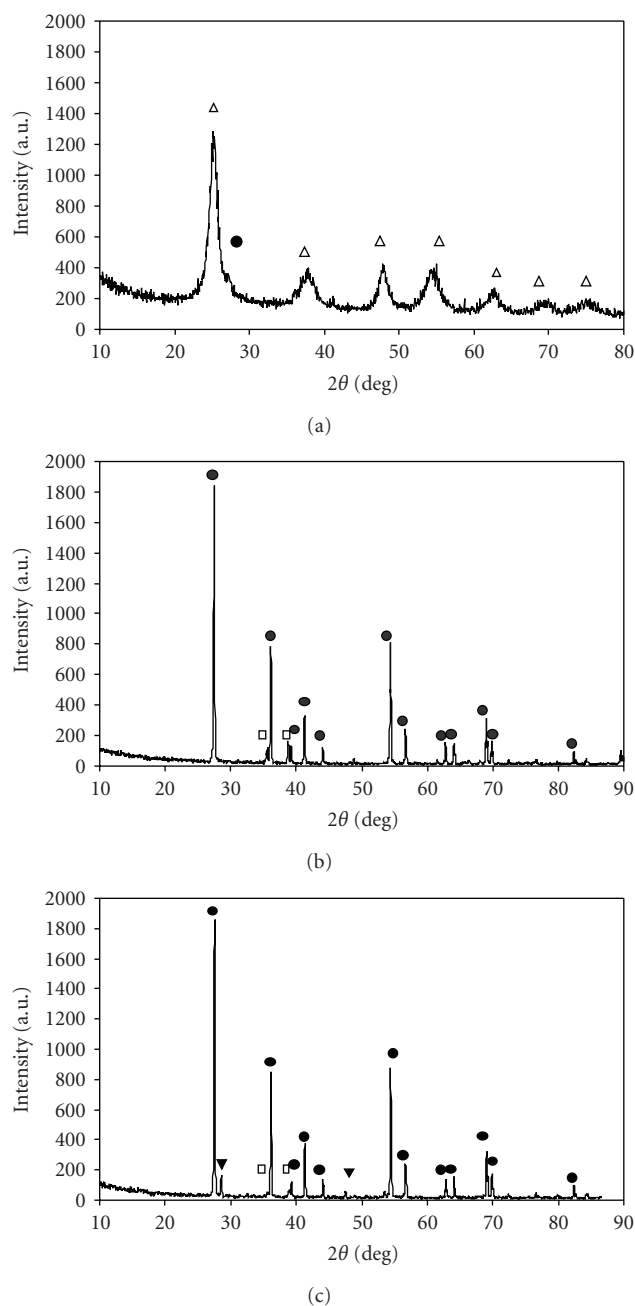


FIGURE 1: XRD patterns of crude TiO₂ and Cu-modified photocatalysts: (a) crude TiO₂; (b) photocatalyst containing 10 wt% Cu; (c) photocatalyst containing 20 wt% Cu. ●-rutile; Δ-anatase; □-CuO; ▼-CuCl.

The crystallite size of rutile calculated on a basis of the Scherrer equation was similar for pure rutile and CuO/rutile catalysts and ranged from 300 to 320 nm, respectively. However, since 100 nm is generally considered the upper limit for XRD crystal size measurements, these data cannot be interpreted as accurate dimensions of the rutile crystals. The only conclusion could be that crystallite sizes of rutile in all of the samples (i.e., pure rutile and CuO/TiO₂) were similar. This might lead to the conclusion that the crystallite size of rutile, being almost the same for all the samples,

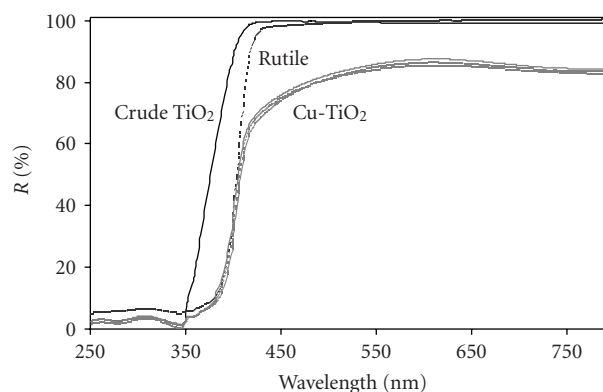


FIGURE 2: UV/Vis-DR spectra of crude TiO₂, rutile and Cu-rutile photocatalysts.

should not affect the photocatalytic behavior of the CuO-modified rutile.

Figure 2 shows UV-Vis/DR spectra of crude TiO₂, rutile and Cu-modified catalysts. It can be observed that all the spectra of CuO-rutile photocatalysts exhibit a similar course and are red shifted for over 30 nm relative to crude TiO₂, what indicates a decrease of the band gap energy. This decrease was associated with phase transformation from anatase to rutile. A similar red shift relative to crude TiO₂ can be observed in case of pure rutile. To determine the band gap energy (E_g) of the samples, the Kubelka-Munk method was used. The E_g values were calculated from the $(F(R)h\nu)^{1/2}$ versus $h\nu$ plots, where $F(R) = (1 - R)/2R$ [26]. The absorption edge for crude TiO₂ was found to be 378 nm, which value corresponded to the band gap energy of $E_g = 3.28$ eV. The absorption edges determined for pure rutile and CuO-rutile samples were 412 and 414 nm, what corresponded to E_g of 3.01 and 2.99 eV, respectively. From Figure 2 it can be also found that CuO-rutile catalysts absorbed more visible light than pure TiO₂. The increased absorption in the Vis region was due to grey color of the CuO-modified photocatalysts.

The TiO₂ and Cu-TiO₂ photocatalysts were applied for the photocatalytic decomposition of acetic acid under N₂ atmosphere. The reaction was conducted for 5 hours. Figure 3 presents changes of concentration of methane in gaseous mixtures versus time of irradiation.

For the initial 2 hours of the process, no significant difference in the amount of methane generated on different catalysts was observed. The concentration of CH₄ was in the range of 0.24–0.28 vol.% what corresponded to 0.12–0.14 mmolCH₄/molCH₃COOH. However, with increasing time of irradiation the differences between the amounts of methane formed with application of different catalysts were becoming more significant. After 5 hours of irradiation the pure rutile was found to be the least efficient catalyst. The amount of methane formed in the presence of rutile was ca. 0.6 vol.%, what corresponded to 0.29 mmolCH₄/molCH₃COOH. The highest amount of methane was generated in case of the catalyst containing 10 wt% of Cu. After 5 hours of irradiation the

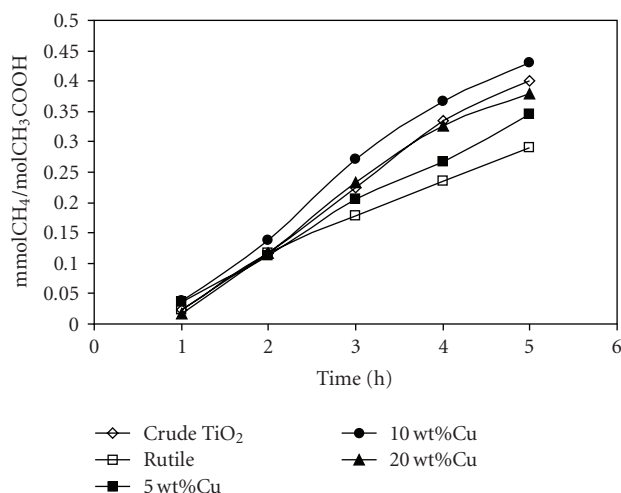


FIGURE 3: Photocatalytic generation of methane on different photocatalysts.

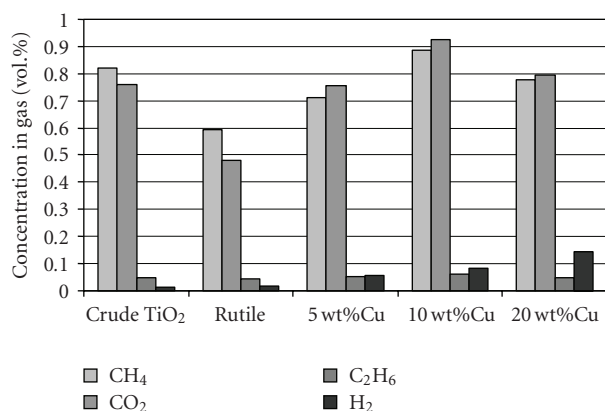


FIGURE 4: A comparison of the amount of products obtained after 5 hours of reaction conducted with different photocatalysts.

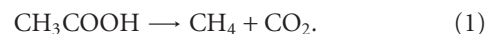
concentration of CH₄ in gaseous mixture was 0.88 vol.% (0.43 mmolCH₄/molCH₃COOH). On the basis of the results presented in Figure 3, the efficiency of the catalysts toward methane generation can be put in the following order: Cu-TiO₂ (10% Cu) > crude TiO₂ ≈ Cu-TiO₂ (20% Cu) > Cu-TiO₂ (5% Cu) > rutile. It should be noticed here that all the rutile catalysts containing CuO were more active than pure rutile. The amount of methane generated on Cu-rutile photocatalyst was higher than that obtained in case of pure rutile for ca. 16, 33 and 24%, for catalysts containing 5–20 wt% of Cu, respectively.

Taking into consideration the above results, the catalyst containing 10 wt% of Cu was further applied in a long term process. Irradiation was conducted for 28 hours. It was found that the amount of methane generated was continuously increasing with increasing time of irradiation. After 5 hours of the process the concentration of methane in gas amounted to 0.88 vol.%, whereas after 28 hours the amount of methane increased up to 3.66 vol.%.

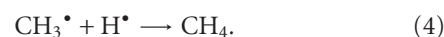
Another gaseous products which were identified in the reaction mixture were carbon dioxide and ethane. Figure 4

shows a comparison of the amount of these compounds generated after 5 hours of irradiation. From the obtained data it was found that the main products of acetic acid decomposition were methane and carbon dioxide. The lowest concentrations of CH₄ and CO₂ in the gaseous mixture were obtained in case of pure rutile, whereas the highest—in case of rutile containing 10 wt% of Cu. The ratio of CH₄/CO₂ formation was found to be in the range of 0.94–0.98 in case of CuO-modified TiO₂, ca. 1.1 in case of crude TiO₂ and about 1.2 for rutile. These data clearly show that for pure TiO₂ the amount of methane was higher than the amount of CO₂. On the contrary in case of the CuO-rutile catalysts the concentration of CO₂ was higher than concentration of CH₄. In Figure 4 it can be also observed that the amount of ethane was significantly lower than the amount of methane and carbon dioxide, regardless of the catalyst used. The lowest concentration of ethane after 5 hours of irradiation was observed for rutile (0.043 vol.%) and the highest for CuO/rutile catalyst containing 10 wt% of Cu (0.062 vol.%). The ratio of CH₄/C₂H₆ was found to be about 14–16.

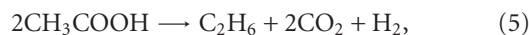
Taking into consideration that the main gaseous products identified were methane and carbon dioxide and that the CH₄/CO₂ ratio was about 1, it might be concluded that the photodecomposition of acetic acid followed the so-called “photo-Kolbe” reaction pathway [15–17]:



Reaction (1) represents the photocatalytic decarboxylation of acetic acid under anaerobic conditions. The reaction is initiated by photogenerated holes and can be also written as follows [27]:



The reaction of the formation of ethane from acetic acid can be presented as follows [18]:



or, taking into consideration the recombination of methyl radicals [27]:



Reactions (5) and (6) in the discussed system are minor ones, what can be concluded on a basis of the obtained data (Figure 4) showing that the amount of ethane was significantly lower than that of methane.

From Figure 4 it can be also found that amongst the gaseous products of the reaction hydrogen was present. Changes of H₂ concentration in time of the experiment are presented in Figure 5. It can be observed that in case of crude TiO₂ and pure rutile the amount of hydrogen was significantly lower than of the Cu-modified photocatalysts. In case of the catalysts containing CuO the H₂ concentration

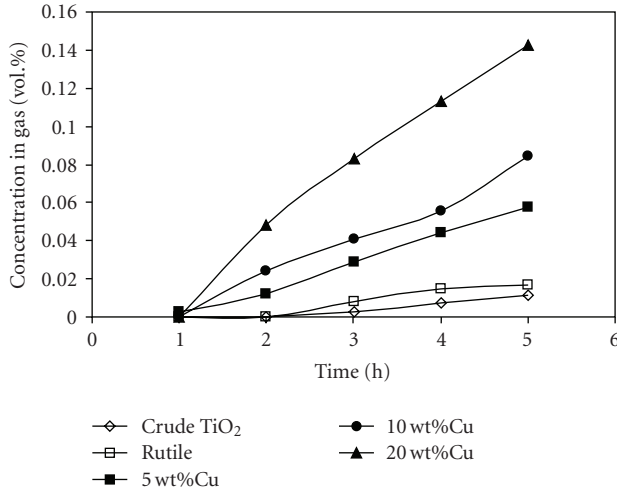
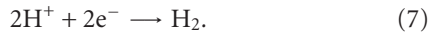


FIGURE 5: Photocatalytic generation of hydrogen on different photocatalysts.

was increasing with increasing Cu loading. After 5 hours of irradiation about 0.06–0.14 vol.% of H₂ was obtained for photocatalysts containing 5–20 wt% of Cu, respectively.

The photocatalytic evolution of hydrogen in the presence of sacrificial agents has been already described in the literature [18, 20–22, 26–34]. In general, when the reducing agent, or hole scavenger, such as alcohol [20, 23, 26–29], organic acid [18, 30, 31] or sulfide ion [32, 33], is present in the solution, the photogenerated holes react with the reducing agent. As a result the photocatalyst is enriched with electrons and H₂ evolution reaction is enhanced [34]:

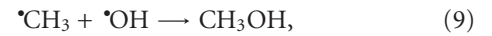


According to Kudo and Miseki [34] the hydrogen evolution in the presence of sacrificial agent does not mean the “water splitting”. Water splitting means to split water into H₂ and O₂ in a stoichiometric amount in the absence of sacrificial reagents [34].

The photocatalytic hydrogen evolution can be enhanced by modification of TiO₂. Literature data [20–23] show that CuO/TiO₂ photocatalysts are very effective in H₂ generation. The TiO₂ acts as the primary catalyst and CuO acts as a cocatalyst, helping charge separation [20]. After absorption of a photon ($h\nu$) with sufficient energy, that is, equal or higher than the band gap energy (E_g) of TiO₂, the electrons and holes are generated. The hole scavenger consumes holes in the valence band rapidly leaving electrons in the conduction band of TiO₂. The conduction band (CB) of CuO is positioned below the CB of TiO₂ which allows transfer of electrons from the CB of TiO₂ to the CB of CuO. These results in a more negative CB potential of CuO and, as a result, enhanced hydrogen evolution. The yield of H₂ evolution greatly relies on the competition between the trapping of the excited electrons by cocatalyst active sites followed by reduction reaction and the electron-hole recombination [23]. As was mentioned earlier, the amount of hydrogen in case of the Cu-modified photocatalysts was significantly higher than in case of pure TiO₂. This might

lead to a conclusion that the limited hydrogen evolution in case of crude TiO₂ and rutile resulted from rapid recombination of holes and electrons, since the separation of electron-hole pairs in case of pure TiO₂ is not as efficient as in the presence of CuO.

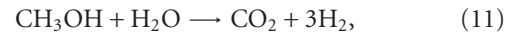
The source of hydrogen in case of the photocatalytic reactions conducted in the presence of sacrificial agents is still under debate. Bandara et al. [20] have argued that H₂ is produced from water. They have drawn such a conclusion on a basis of the experiment performed with application of absolute methanol. During this process no H₂ evolution was observed. On the other hand, Sakata et al. [18] proposed that H₂ formation is due to photocatalytic decomposition of acetic acid:



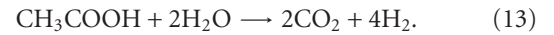
or



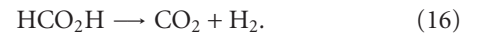
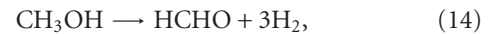
In the next step, CH₃OH and HOCH₂COOH are decomposed into carbon dioxide and hydrogen:



The overall reaction summarizing (8)–(12) can be written as follows:



The photocatalytic decomposition of methanol was also presented as follows [29]:



From the mechanism proposed by Sakata et al. [18] it can be found that H₂ is produced from methanol and glycolic acid, which are formed from acetic acid ((9) and (10)). These two reactions are possible when hydroxyl radicals are present in the solution. However, in the low pH region the amount of OH[•] radicals formed is not high due to low concentration of OH[−]. Therefore, the amount of methanol and glycolic acid which might be produced in the reactions (9) and (10) should be rather low. This leads to a conclusion that in the low pH region the reaction (13) is of minor importance [18]. In view of this, it is more probable that the hydrogen ions come mainly from decomposition of acetic acid presented by (8), rather than from decomposition of methanol or glycolic acid (reactions (11) and (12)). Water could be also involved in H₂ generation through the reaction (7), however, according to Jang et al. [33] its effect should be insignificant due to the low concentration of protons in neutral water. Summing up, the photocatalytic evolution of H₂ in the

presence of acetic acid as a sacrificial agent was probably mainly due to reduction of protons (H^+) generated during decomposition of CH_3COOH (8). Moreover, it can be also supposed that some amount of hydrogen was generated from by-products of acetic acid decomposition, such as methanol and glycolic acid, as well as from water molecules. However, the H_2 evolution during the latter two processes compared to the overall hydrogen evolution is supposed to be of minor importance.

An evidence for the supposition that the source of hydrogen is acetic acid, not water, might be also the ratio of methane to carbon dioxide concentrations (Figure 4). As was mentioned earlier, in case of crude TiO_2 and rutile the amount of methane was higher than the amount of CO_2 , whereas for $CuO-TiO_2$ catalysts the concentration of CH_4 was lower than CO_2 . This might suggest that in case of these two types of photocatalysts some other reactions, despite of those described by (1)–(6) took place. One explanation might be generation of hydrogen from acetic acid. Assuming that both, methane and at least part of the hydrogen were produced from acetic acid, the amounts of these compounds should depend on the efficiency of the reactions of their formation. Thus, the higher amount of H_2 , the lower amount of CH_4 should be generated, since H^+ would take part in reaction (7) instead of (1)–(4). In case of pure TiO_2 the amount of H_2 was very low and therefore the CH_4/CO_2 ratio was above 1. For the $CuO-TiO_2$ catalysts higher amount of hydrogen was generated, what might be supposed to be a reason of a decrease of CH_4 concentration. Moreover, the effect of C_2H_6 and possibly higher hydrocarbons formation on methane concentration in the reaction mixture should be also taken into consideration. However, taking into account that the amount of C_2H_6 was comparable for all the catalysts used (0.02–0.03 mmol C_2H_6 /mol CH_3COOH after 5 hours of irradiation) the effect of ethane generation on CH_4/CO_2 ratio seems to be of lower importance. Besides, it might be also supposed that a certain amount of carbon dioxide was reduced to CH_4 , what might be concluded from the fact that the concentration of CO_2 in case of crude TiO_2 and rutile was lower than that of methane. Literature data [3, 8, 9, 35] show that the reduction of carbon dioxide in the presence of various types of modified TiO_2 is possible. However, in order to state unequivocally what affects the CH_4/CO_2 ratio in the presence of pure TiO_2 and CuO/TiO_2 catalysts, further investigations are necessary.

Summing up, from the presented data (Figures 3 and 4) it can be clearly seen that the most active photocatalyst towards hydrocarbons (i.e., methane and ethane) generation was $Cu-TiO_2$ containing 10 wt% Cu. Since the crystallite size of rutile in all of the Cu-modified photocatalysts as well as in pure rutile could be assumed to be comparable, it might be supposed that the highest photoactivity of $Cu-TiO_2$ (10% Cu) was associated with the amount of CuO present in this sample. The photocatalytic activity of rutile-type samples increased as follows: pure rutile < $Cu-TiO_2$ (5% Cu) < $Cu-TiO_2$ (10% Cu), what suggests that 5 wt% of Cu was below the optimum value. Taking into consideration that in case of the $Cu-TiO_2$ containing 20 wt% Cu the yield of CH_4 formation decreased, one might draw a conclusion

that this sample was overloaded with CuO. This overloading might have led to a “shading effect” of CuO [3], which means that particles of copper oxide covered most of active sites of titania. As a result, the TiO_2 surface accessible to acetic acid molecules decreased and the yield of the “photo-Kolbe” reaction also decreased. However, the efficiency of photocatalysts toward hydrogen evolution (Figures 4 and 5) was as follows: $Cu-TiO_2$ (20% Cu) > $Cu-TiO_2$ (10% Cu) > $Cu-TiO_2$ (5% Cu) > rutile \approx crude TiO_2 . These results show that the catalyst which was the most effective in methane production (i.e., containing 10 wt% Cu) was the second one in case of hydrogen generation. Therefore, the explanation about “shading effect” of CuO in case of the catalyst containing 20 wt% Cu seems to be unsatisfactory. In view of these, more probable explanation is that at higher CuO content, higher amount of acetic acid molecules took place in the reaction of H_2 formation rather than CH_4 generation. Therefore, since the amount of substrate, that is, CH_3COOH , was always the same, the increased production of hydrogen should lead to a decreased production of methane, what was observed in the discussed experiments.

4. Conclusions

It was found that it is possible to generate useful hydrocarbons, such as CH_4 and C_2H_6 , from acetic acid in the presence of Cu-modified rutile under UV irradiation. The efficiency of the catalysts toward methane generation changed in the following order: $Cu-TiO_2$ (10% Cu) > crude $TiO_2 \approx Cu-TiO_2$ (20% Cu) > $Cu-TiO_2$ (5% Cu) > rutile. The amount of CH_4 produced in the presence of the catalyst containing 10 wt% of Cu was higher for ca. 7% than in case of crude anatase-phase TiO_2 and for ca. 33% than in case of pure rutile. The concentration of ethane was 14–16 times lower than the amount of methane. The lowest concentration of C_2H_6 after 5 hours of irradiation was observed for rutile (0.043 vol.%) and the highest for CuO /rutile catalyst containing 10 wt% of Cu (0.062 vol.%). The mechanism of methane generation from acetic acid followed the photo-Kolbe reaction pathway, what was concluded on a basis of CH_4/CO_2 ratio, which was found to be ~ 1 . Low concentrations of hydrogen were also detected in the gaseous mixtures. The amount of H_2 was increasing with increasing Cu loading. After 5 hours of irradiation about 0.06–0.14 vol.% of H_2 was obtained for photocatalysts containing 5–20 wt% of Cu, respectively. On the basis of the experimental data it is supposed that the source of hydrogen was acetic acid, not water.

Further investigations on the effectiveness of methane generation in the presence of CuO/TiO_2 photocatalyst are in progress.

Acknowledgments

This work has been supported by the Polish Ministry of Science and Higher Education as a scientific project no. N523 413435 (2008–2011). The author wish to thank Professor A. W. Morawski, Head of the Institute of Chemical and Environment Engineering for precious advices and creative discussion during preparation of this article.

References

- [1] G. Lastella, C. Testa, G. Cornacchia, M. Notornicola, F. Voltasio, and V. K. Sharma, "Anaerobic digestion of semi-solid organic waste: biogas production and its purification," *Energy Conversion and Management*, vol. 43, no. 1, pp. 63–75, 2002.
- [2] V. Augugliaro, M. Litter, L. Palmisano, and J. Soria, "The combination of heterogeneous photocatalysis with chemical and physical operations: a tool for improving the photoprocess performance scale for the treatment of biorecalcitrant pollutants," *Journal of Photochemistry and Photobiology C*, vol. 7, no. 4, pp. 127–144, 2006.
- [3] Slamet, H. W. Nasution, E. Purnama, S. Kosela, and J. Gunlazuardi, "Photocatalytic reduction of CO₂ on copper-doped Titania catalysts prepared by improved-impregnation method," *Catalysis Communications*, vol. 6, no. 5, pp. 313–319, 2005.
- [4] K. Kočí, L. Obalová, and Z. Lacný, "Photocatalytic reduction of CO₂ over TiO₂ based catalysts," *Chemical Papers*, vol. 62, no. 1, pp. 1–9, 2008.
- [5] S. S. Tan, L. Zou, and E. Hu, "Photosynthesis of hydrogen and methane as key components for clean energy system," *Science and Technology of Advanced Materials*, vol. 8, no. 1-2, pp. 89–92, 2007.
- [6] C.-C. Lo, C.-H. Hung, C.-S. Yuan, and J.-F. Wu, "Photoreduction of carbon dioxide with H₂ and H₂O over TiO₂ and ZrO₂ in a circulated photocatalytic reactor," *Solar Energy Materials and Solar Cells*, vol. 91, no. 19, pp. 1765–1774, 2007.
- [7] Y. Shiraishi and T. Hirai, "Selective organic transformations on titanium oxide-based photocatalysts," *Journal of Photochemistry and Photobiology C*, vol. 9, no. 4, pp. 157–170, 2008.
- [8] I.-H. Tseng, J. C. S. Wu, and H.-Y. Chou, "Effects of sol-gel procedures on the photocatalysis of Cu/TiO₂ in CO₂ photoreduction," *Journal of Catalysis*, vol. 221, no. 2, pp. 432–440, 2004.
- [9] I.-H. Tseng, W.-C. Chang, and J. C. S. Wu, "Photoreduction of CO₂ using sol-gel derived titania and titania-supported copper catalysts," *Applied Catalysis B*, vol. 37, no. 1, pp. 37–48, 2002.
- [10] G. Guan, T. Kida, and A. Yoshida, "Reduction of carbon dioxide with water under concentrated sunlight using photocatalyst combined with Fe-based catalyst," *Applied Catalysis B*, vol. 41, no. 4, pp. 387–396, 2003.
- [11] N. Sasirekha, S. J. S. Basha, and K. Shanthi, "Photocatalytic performance of Ru doped anatase mounted on silica for reduction of carbon dioxide," *Applied Catalysis B*, vol. 62, no. 1-2, pp. 169–180, 2006.
- [12] S. S. Tan, L. Zou, and E. Hu, "Photocatalytic reduction of carbon dioxide into gaseous hydrocarbon using TiO₂ pellets," *Catalysis Today*, vol. 115, no. 1–4, pp. 269–273, 2006.
- [13] H. Yamashita, Y. Fujii, Y. Ichihashi, et al., "Selective formation of CH₃OH in the photocatalytic reduction of CO₂ with H₂O on titanium oxides highly dispersed within zeolites and mesoporous molecular sieves," *Catalysis Today*, vol. 45, no. 1–4, pp. 221–227, 1998.
- [14] O. Ozcan, F. Yukruk, E. U. Akkaya, and D. Uner, "Dye sensitized artificial photosynthesis in the gas phase over thin and thick TiO₂ films under UV and visible light irradiation," *Applied Catalysis B*, vol. 71, no. 3-4, pp. 291–297, 2007.
- [15] B. Kraeutler and A. J. Bard, "Photoelectrosynthesis of ethane from acetate ion at an *n*-type TiO₂ electrode. The photo-Kolbe reaction," *Journal of the American Chemical Society*, vol. 99, no. 23, pp. 7729–7731, 1977.
- [16] B. Kraeutler and A. J. Bard, "Heterogenous photocatalytic synthesis of methane from acetic acid—new Kolbe reaction pathway," *Journal of the American Chemical Society*, vol. 100, no. 7, pp. 2239–2240, 1978.
- [17] B. Kraeutler, C. D. Jaeger, and A. J. Bard, "Direct observation of radical intermediates in the photo-Kolbe reaction—heterogenous photocatalytic radical formation by electron spin resonance," *Journal of the American Chemical Society*, vol. 100, no. 15, pp. 4903–4905, 1978.
- [18] T. Sakata, T. Kawai, and K. Hashimoto, "Heterogeneous photocatalytic reactions of organic acids and water. New reaction paths besides the photo-Kolbe reaction," *Journal of Physical Chemistry*, vol. 88, no. 11, pp. 2344–2350, 1984.
- [19] G. R. Dey and K. K. Pushpa, "Methane generated during photocatalytic redox reaction of alcohols on TiO₂ suspension in aqueous solutions," *Research on Chemical Intermediates*, vol. 32, no. 8, pp. 725–736, 2006.
- [20] J. Bandara, C. P. K. Udawatta, and C. S. K. Rajapakse, "Highly stable CuO incorporated TiO₂ catalyst for photocatalytic hydrogen production from H₂O," *Photochemical and Photobiological Sciences*, vol. 4, no. 11, pp. 857–861, 2005.
- [21] Z. Jin, X. Zhang, Y. Li, S. Li, and G. Lu, "5.1% apparent quantum efficiency for stable hydrogen generation over eosin-sensitized CuO/TiO₂ photocatalyst under visible light irradiation," *Catalysis Communications*, vol. 8, no. 8, pp. 1267–1273, 2007.
- [22] H.-J. Choi and M. Kang, "Hydrogen production from methanol/water photodecomposition over the Cu loaded TiO₂," *Applied Chemistry*, vol. 10, no. 2, pp. 453–456, 2006.
- [23] T. Sreethawong and S. Yoshikawa, "Comparative investigation on photocatalytic hydrogen evolution over Cu-, Pd-, and Au-loaded mesoporous TiO₂ photocatalysts," *Catalysis Communications*, vol. 6, no. 10, pp. 661–668, 2005.
- [24] S. Mozia, "Effect of calcination temperature on photocatalytic activity of TiO₂. Photodecomposition of mono- and polyazo dyes in water," *Polish Journal of Chemical Technology*, vol. 10, no. 3, pp. 42–49, 2008.
- [25] M. S. P. Francisco and V. R. Mastelaro, "Inhibition of the anatase-rutile phase transformation with addition of CeO₂ to CuO-TiO₂ system: Raman spectroscopy, X-ray diffraction, and textural studies," *Chemistry of Materials*, vol. 14, no. 6, pp. 2514–2518, 2002.
- [26] N. Todorova, T. Giannakopoulou, G. Romanos, T. Vaimakis, J. Yu, and C. Trapalis, "Preparation of fluorine-doped TiO₂ photocatalysts with controlled crystalline structure," *International Journal of Photoenergy*, vol. 2008, Article ID 534038, 9 pages, 2008.
- [27] M. Subrahmanyam, S. Kaneco, and N. Alonso-Vante, "A screening for the photo reduction of carbon dioxide supported on metal oxide catalysts for C₁–C₃ selectivity," *Applied Catalysis B*, vol. 23, no. 2-3, pp. 169–174, 1999.
- [28] M.-K. Jeon, J.-W. Park, and M. Kang, "Hydrogen production from methanol/water decomposition in a liquid photosystem using the anatase and rutile forms of Cu-TiO₂," *Journal of Industrial and Engineering Chemistry*, vol. 13, no. 1, pp. 84–91, 2007.
- [29] T. Kawai and T. Sakata, "Photocatalytic hydrogen production from liquid methanol and water," *Journal of the Chemical Society, Chemical Communications*, no. 15, pp. 694–695, 1980.
- [30] B. Zielińska, J. Sreńscek-Nazzal, and R. J. Kaleńczuk, "Photocatalytic hydrogen generation over alkali niobates in the presence of organic compounds," *Polish Journal of Chemical Technology*, vol. 10, no. 4, pp. 1–3, 2008.

- [31] B. Zielińska, E. Borowiak-Paleń, and R. J. Kaleńczuk, "Photocatalytic hydrogen generation over alkaline-earth titanates in the presence of electron donors," *International Journal of Hydrogen Energy*, vol. 33, no. 7, pp. 1797–1802, 2008.
- [32] K. G. Kanade, B. B. Kale, J.-O. Baeg, et al., "Self-assembled aligned Cdoped ZnO nanoparticles for photocatalytic hydrogen production under visible light irradiation," *Materials Chemistry and Physics*, vol. 102, no. 1, pp. 98–104, 2007.
- [33] J. S. Jang, H. G. Kim, P. H. Borse, and J. S. Lee, "Simultaneous hydrogen production and decomposition of H_2S dissolved in alkaline water over CdS.TiO_2 composite photocatalysts under visible light irradiation," *International Journal of Hydrogen Energy*, vol. 32, no. 18, pp. 4786–4791, 2007.
- [34] A. Kudo and Y. Miseki, "Heterogeneous photocatalyst materials for water splitting," *Chemical Society Reviews*, vol. 38, no. 1, pp. 253–278, 2009.
- [35] M. Anpo, H. Yamashita, Y. Ichihashi, and S. Ehara, "Photocatalytic reduction of CO_2 with H_2O on various titanium oxide catalysts," *Journal of Electroanalytical Chemistry*, vol. 396, no. 1-2, pp. 21–26, 1995.