The influence of the addition of carbon spheres on photoactivity of TiO_2 and ZnO in CO_2 reduction process

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ABSTRACT

The development of an effective photocatalyst for CO_2 reduction is currently being addressed by many scientists. This study concerns the influence of the addition of carbon spheres (CS) on photoactivity of TiO_2 and ZnO. The photocatalysts were tested in a liquid phase system in an alkaline environment. The suspensions of the tested materials were irradiated with UV–Vis light for 6 h. Then, the amount of the obtained products in the gas phase was analysed by gas chromatography. The identified products of CO_2 photoreduction were hydrogen, carbon monoxide, and methane. Based on the results, it was found that CS/TiO_2 and CS/ZnO showed similar activity in carbon dioxide reduction processes, however, more product amounts were obtained in experiments with the use of CS/TiO_2 materials. The addition of carbon spheres to titanium dioxide improved its activity in carbon monoxide production. The maximum photoactivity of CS/TiO_2 was observed for the addition of 0.1 g of CS. On the other hand, in the case of CS/ZnO materials, carbon spheres did not positively affect their performance. Nevertheless, their activity increased with the CS amount.

1. Introduction

In the face of current dangerous climate changes, the photoreduction of CO_2 into valuable products is one of the most promising methods to protect our environment. But, at the same time, it is a very complex process influenced by many parameters. That is why scientists from all over the world are intensively studying this challenging issue.

The CO_2 molecule is thermodynamically stable [1], so any reaction with it requires a significant amount of energy. Therefore, the conditions for photocatalysis, e.g., the type of photocatalyst, its size and sorption properties, the type of system, pH, temperature, intensity and range of radiation, are crucial to achieving a high level of CO_2 reduction.

The selection of the photocatalyst plays an important role here. TiO_2 is the most commonly used in photocatalysis, not only in carbon dioxide reduction but also in organic pollutants degradation, dye bleaching, or air and water purification in general [2–7]. Its P25 type, composed of 75% anatase and 25% rutile, is highly effective for photocatalytic processes and is more active than single–phase TiO_2 [8,9]. Titanium dioxide in the form of brookite has been characterized by even higher photoactivity [10–12]. There are many publications concerning CO_2 reduction

processes in which titanium dioxide in various forms is employed [13–17].

Aside from titanium dioxide, ZnO is considered a material with similar properties. According to the literature, it has a strong electron–migration ability, high exciton binding energy, and the ability to generate electron–hole pairs rapidly [18]. Unfortunately, it has a relatively large band gap. Hence it needs to be activated with UV light [19–21]. The poor ability to absorb visible light significantly limits the application of ZnO in more economical solutions that use sunlight. It is most commonly used to remove detergents, dyes, and pesticides [22–26]. However, publications concerning CO_2 photoreduction can be found as well [27,28]. According to the literature, ZnO can also be successfully used in CO2 electroreduction processes [29–31].

Both TiO_2 and ZnO are characterized by non–toxicity and relatively low production costs. Based on the literature, combining those two compounds is a promising method of increasing the activity in photocatalytic processes due to the synergistic effect of TiO_2 and ZnO properties required in CO_2 photoreduction [32]. Other photocatalysts studied and described in detail in the literature include carbonaceous materials (mainly g–C3N4 and its composites [33–35]), salts composites

(e.g. CdS, ZnS, MoS_2 [36–41]), or Layered Double Hydroxides (LDHs) [42–44]. The main products in the photocatalytic reduction of CO2 with the use of those materials are carbon monoxide [36–38,43,44], methane [36–40,43], hydrogen [38,44], methanol [40–42], and formic acid [33].

Another critical factor in CO_2 photoreduction is the reactor configuration and process conditions. Currently, two types of setups are widely used, namely liquid–phase reactors, which have been known and developed for decades, and gas–phase reactors, which are newer and characterized by high efficiency [45]. The main disadvantages of liquid–phase reactors include poor solubility of CO_2 solubility in water, limited mass transfer, and agglomeration of the catalyst [46,47]. This can lead to a significant reduction in photocatalytic performance. However, the undesirable effects can be minimized, especially by using circulation, constant stirring, and solvents/reduction agents other than water [45,48,49].

As mentioned above, the stability of the carbon dioxide molecule makes it difficult to carry out the photocatalytic process. In this case, it is worth considering the process in an alkaline environment. The absorption of carbon dioxide in an aqueous solution of sodium hydroxide is a recognized method of CO_2 capture described in the scientific literature [50–53]. It is also well–known that the solubility of carbon dioxide in an aqueous NaOH solution is higher than in water. This is related to the carbonate equilibria, which means that CO_2 is present in different forms depending on the pH of the solution [54]:

- dissolved CO_2/carbonate acid ($H_2CO_{3(aq)}$) at pH below 6.3, which is rapidly desorbed into the gas phase;
- bicarbonate ions (HCO^{3-}), which predominate at pH between 6.3 and 10.3;
- carbonate ions (CO_3^{2-}) are only present in a strongly alkaline environment at pH values above 10.3.

Carbonate and bicarbonate ions are more reactive than CO_2 itself. Moreover, OH^- ions from NaOH solution can be hole–scavenging and form hydroxyl radicals that prevent the recombination of hole–electron pairs [55]. In another publication [56], thanks to this property, we demonstrated that more hydrogen is produced in an alkaline environment than in aqueous (neutral) conditions.

The adsorption of CO_2 is another key factor in the photoreduction process. A good CO_2 adsorption capacity means that more CO_2 molecules can participate in the reaction on the surface of the photocatalyst. During the adsorption process, a negatively charged $CO_2^{\delta-}$ molecule is formed, a crucial intermediate product in the formation of other products of the CO_2 photoreduction process [57].

Considering the above information, experiments were carried out to investigate the photocatalytic properties in the process of CO_2 reduction in the liquid phase. The tested materials consisted of TiO_2 and ZnO, known as photoactive materials, and carbon spheres (CS) with excellent CO_2 adsorption properties and high surface area (S_{BET}). The aim was to achieve a synergistic effect of photocatalysts with carbon spheres by combining the two components with specific properties and comparing the activities of the two groups of materials tested, which were CS/TiO_2 and CS/ZnO. Through this combination, we expected to achieve enhanced CO_2 adsorption, which is crucial for the photocatalytic reduction of carbon dioxide.

2. Materials and methods

2.1. Samples preparation

The following materials were used to prepare photocatalysts: P25 type TiO_2 (AEROXIDE® TiO_2 P25, Evonik Industries AG, Germany), ZnO with particle size < 100 nm (Sigma–Aldrich, USA), and carbon spheres obtained using resorcinol and formaldehyde. A detailed description of the synthesis of carbon spheres has been described in our previous publication [58]. The mixtures of titanium dioxide or zinc oxide with

carbon spheres were prepared using a microwave–assisted solvothermal reactor (Ertec, Poland), as described elsewhere [59]. The obtained materials were ground in a mortar, and then their photocatalytic properties were assessed. 0.2 M aqueous NaOH solution was prepared from reagent–grade sodium hydroxide (Avantor Performance Materials, Poland) and distilled water.

2.2. Specific surface area, total pore volume and adsorption capacity measurements

Surface properties were determined using N_2 adsorption/desorption isotherms performed on a QUADRASORB evoTM Gas Sorption automatic system (Quantachrome Instruments, Boynton Beach, FL, USA) at − 196 °C. Before each adsorption experiment, samples were outgassed at 250 °C under a vacuum of 1×10^{-5} mbar for 12 h using a MasterPrep multi-zone flow/vacuum degasser from Quantachrome Instruments to remove adsorbed species that could intervene in the adsorption processes. The surface area (S_{BET}) was determined in the relative pressure range of 0.05–0.3 and calculated based on Brunauer–Emmett–Teller (BET) equation. The total pore volume (TPV) was calculated from the volume of nitrogen held at the highest relative pressure ($p/p_0 = 0.99$). Pore size distributions (PSD) of the samples were determined from CO_2 adsorption isotherms at 0 °C by integrating the pore volume distribution function using the NLDFT method.

Carbon dioxide adsorption isotherms at 25 °C were measured with Quadrasorb™ automatic system (Quantachrome Instruments, Boynton Beach, FL, USA) in the pressure range between 0.01 and 0.98 bar.

2.3. Zeta potential and average particle size measurements

The zeta potential of the samples was measured using Zetasizer Nano–ZS (Malvern Instruments Ltd. Malvern, UK). The measurements were performed at a pH of 6.9, corresponding to a pH in a given process environment.

The average particle size of TiO_2 and ZnO was determined using the same instrument. The measurements were carried out for samples dispersed in ultrapure water.

2.4. SEM analysis

The surface morphology of the samples was investigated with a scanning electron microscope (SEM Hitachi SU8020, Japan) with an acceleration voltage of 5.0 kV, and magnitude of 45.0k and 50.0k.

2.5. Photocatalytic process

The experiments were performed in a liquid–phase bottle–shaped reactor. The working volume of the reactor was 766 cm^3. A 150 W medium–pressure mercury lamp TQ150 Z3 (Heraeus, Germany) was used in the tests. It was characterized by a wide range of UV–Vis light, with an intense peak at about 365 nm (UV–A radiation). As presented in the scheme, the lamp was placed in a quartz condenser inside the reactor, (Fig. 1). It was constantly cooled with fresh water. The reactor was placed in the thermostatic chamber to maintain a stable temperature and exclude any light sources.

The photocatalytic processes were prepared as follows: 500 cm^3 of 0.2 M aqueous NaOH solution was poured into the reactor. Then 200 mg of the tested material was added. The mixture was saturated with pure CO_2 (Messer, Poland) for 16 h. Then, the system was closed, and the lamp was turned on. The suspension of the photocatalyst was constantly stirred with the use of the magnetic stirrer and the pump (flow rate of 1.6 dm^3/h). The processes were performed at 20 °C and lasted for 6 h. The gas samples for analysis were collected every 1 h.
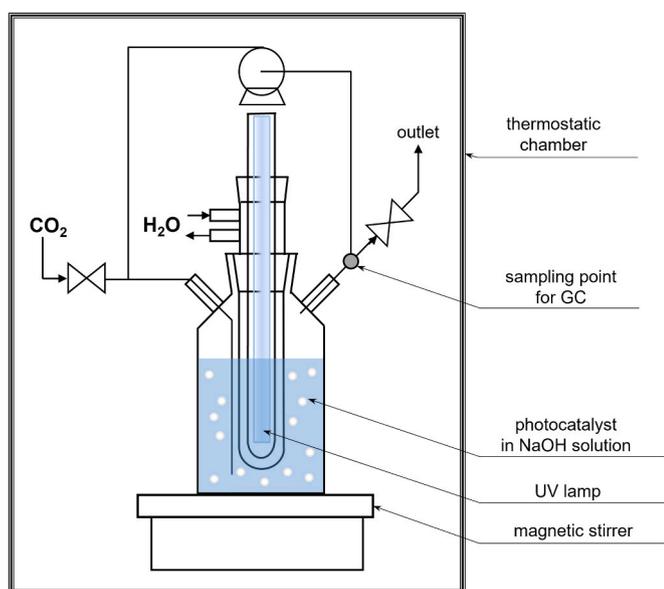
Fig. 1. Scheme of the reactor for photocatalytic process in a liquid phase.

2.6. Gas phase analysis

The gas phase composition was analyzed using a Master GC chromatograph (DANI Instruments, Italy) equipped with micropacked Shincarbon ST 100/120 column. The analyses were performed using TCD and FID detectors. The methanizer was placed between the detectors. It converted the inorganic product (carbon monoxide) to methane, allowing us to accurately determine its amount using FID. The carrier gas was argon. The volume of the analyzed gas sample was 1 cm^3. The amount of hydrogen, carbon monoxide and methane in a gas phase was calculated based on the calibration curve.

3. Results and discussion

In our previously works, the textural and adsorption properties of carbon spheres and carbon spheres/metal oxides composites [59–61] were studied. In Figs. 2 and 3, CO_2 adsorption isotherms are presented for the composites based on carbon spheres and titanium dioxide and zinc oxide, respectively. It is clearly shown that together with the

Fig. 3. CO_2 sorption isotherms of the obtained CS/ZnO composites.

increase of the carbon content in the materials higher values of CO_2 adsorption were recorded. CO_2 adsorption at 25 °C was the highest for the samples with the addition of 1.00 g of CS, and it ranged 1.22 mmol/g and 1.11 mmol/g for materials containing TiO_2 and ZnO, respectively. It was found that for all the studied samples slightly lower values of CO_2 adsorption were observed for the composites with addition of zinc oxide, regardless of the ratio of metal oxide to carbon in the obtained materials. From the available papers [62–65] it is known that in the adsorption of carbon dioxide not only the values of surface area or total pore volume is important, but above all the smallest pores, below 0.7 nm are responsible for this process. In Fig. 4 the comparison between the pore size distributions of the obtained materials is presented. It was found that the content of ultramicropores increased together with the increase of content of carbon for two types of materials. Additionally it was noticed that slightly lower volumes of micropores and ultramicropores were obtained in the case of the samples modified with zinc oxide and therefore slightly lower values of CO_2 adsorption were noticed for this type of the samples. Detailed characteristics of the textural properties of the obtained composites have been presented in the paper [59].

The experimentally determined zeta potentials at pH = 6.9 (the same

Fig. 2. CO_2 sorption isotherms of the obtained CS/TiO_2 composites.
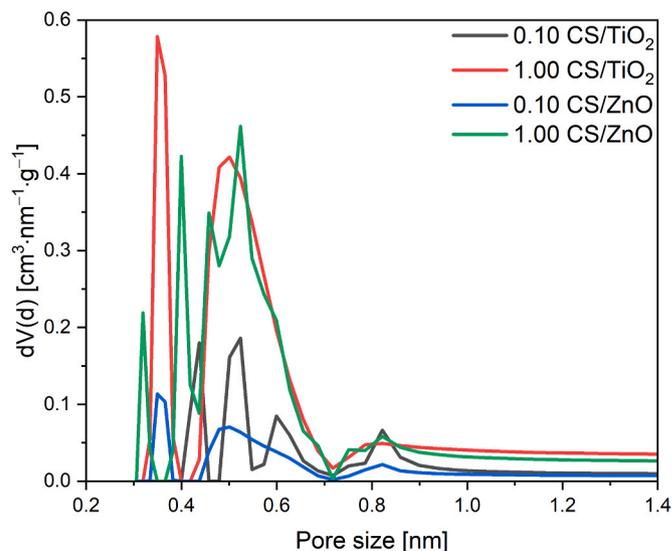
Fig. 4. Comparison of the pore size distributions of the CS/TiO_2 and CS/ZnO composites with the lowest and the highest content of carbon.

as in the photoreactor after saturation with CO_2) were negative for all base materials, and range from -9.2 mV to -19.9 mV. From the results, it can be concluded that ZnO had a less negative ζ–potential in a given environment than CS. Therefore, the repulsive forces between the particles of these two materials were weaker than in the samples containing CS and TiO_2, with the zeta potential of titanium dioxide being higher than that of carbon spheres. This could affect the transfer of electrons and also CO_2 molecules between the adsorbent and the photocatalysts. The average particle size was similar for TiO_2 and ZnO (136.2 nm and 92.5 nm, respectively), while carbon spheres were characterized by the largest value of this parameter (471.2 nm). The differences in size between an active material and the adsorbent can be seen in Fig. 5. In the SEM images shown, it can be observed that the carbon spheres are much larger in size than the photocatalysts particles. It can also be seen that TiO_2 and ZnO form agglomerates on the surface of the carbon spheres. In addition, they differ in shape. While TiO_2 is fine and rather spherical, ZnO has an elongated appearance.

The starting materials (shown in Table 1) and their mixtures with different ratios of CS to TiO_2/ZnO were tested for their photocatalytic properties in the photocatalytic reduction of CO_2 in the liquid phase, using a suspension of the tested material in a 0.2 M NaOH solution, as described in Section 2.5. It should be emphasized that the purpose of the experiments was to verify whether, after mixing materials commonly used as photocatalysts and carbon spheres with good adsorption properties and a developed specific surface area, a synergistic effect occurs and the amounts of the obtained products will be higher due to the increased ability to adsorb CO_2 and thus a longer contact time between the carbon dioxide molecule and the surface of the photocatalysts.

The CO_2 photoreduction products identified during the process are hydrogen, carbon monoxide, and methane. They can be formed in the following reactions [67–69]:

- water splitting, which is a two–electrons reaction and is the first necessary step in CO_2 reduction, hydrogen is formed:

$$H_2O + 2h^+ \rightarrow \tfrac{1}{2}O_2 + 2H^+ \tag{1}$$

$$2H^+ + 2e^- \rightarrow H_2 \tag{2}$$

the two–electron reduction of CO_2, leading to the formation of the main product, namely carbon monoxide:

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \tag{3}$$

- the eight–electron reaction that requires the most energy and produces methane:

Table 1
The selected properties of base materials [59,66].

Material	Properties				
	S_{BET} [m²/g]	TPV [cm³/g]	CO_2 25 °C [mmol/g]	ζ–potential [mV]	Average particle size [nm]
CS	455	0.26	2.43	−13.4	417.2
P25 TiO₂	54	0.40	0.16	−19.9	136.2
ZnO	11	0.03	0.04	−9.2	92.5

S_{BET} – specific surface area; **TPV** – total pore volume; **CO_2 0 °C** – CO_2 sorption capacity at 0 °C; **CO_2 25 °C** – CO_2 sorption capacity at 25 °C; **ζ–potential** – zeta potential at pH = 6.9

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \tag{4}$$

These products are characterized by poor solubility in liquids and immediately desorb from the liquid phase to the gas phase after formation. Therefore, their analysis was performed only in the gas phase.

Table 2
Materials tested in photocatalytic reduction of CO_2.

Material acronym	Mass ratio of carbon spheres to TiO_2 or ZnO	Mass of the material in the reactor [g]	Mass of pure TiO_2 or ZnO in the reactor [g]
TiO₂	0.00: 1.00	0.200	0.200
0.05 CS/TiO₂	0.05: 1.00	0.204	0.194
0.10 CS/TiO₂	0.10: 1.00	0.206	0.188
0.25 CS/TiO₂	0.25: 1.00	0.204	0.164
0.50 CS/TiO₂	0.50: 1.00	0.199	0.133
1.00 CS/TiO₂	1.00: 1.00	0.203	0.102
ZnO	0.00: 1.00	0.202	0.202
0.05 CS/ZnO	0.05: 1.00	0.202	0.192
0.10 CS/ZnO	0.10: 1.00	0.201	0.183
0.25 CS/ZnO	0.25: 1.00	0.203	0.163
0.50 CS/ZnO	0.50: 1.00	0.201	0.134
1.00 CS/ZnO	1.00: 1.00	0.205	0.103
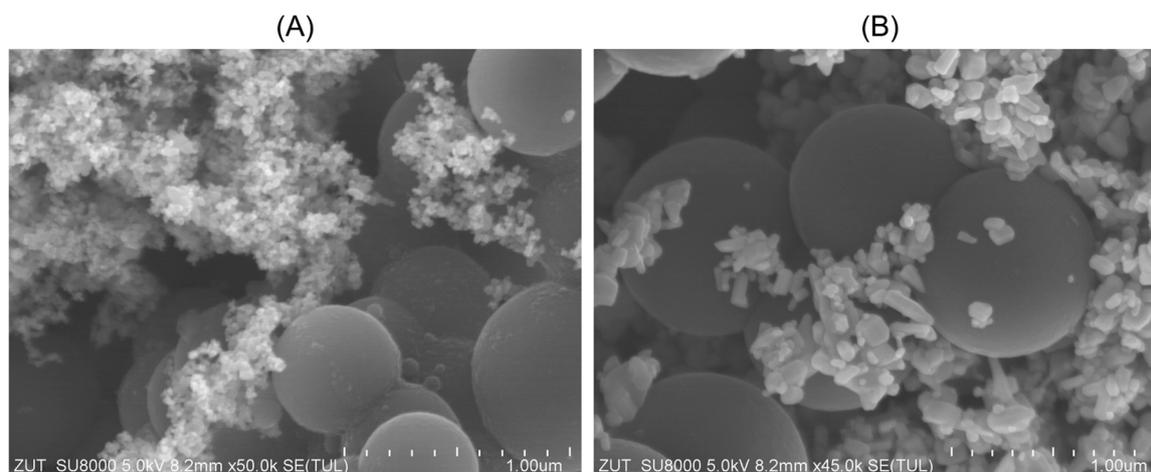
Fig. 5. SEM images of: (A) 0.50 CS/TiO_2; (B) 0.50 CS/ZnO.

The results obtained are discussed below.

The data of the tested samples are listed in Table 2. 12 experiments were performed with mixtures of TiO_2 or ZnO with carbon spheres (CS). For both groups of materials, samples were obtained with mass ratios of CS to TiO_2 or ZnO ranging from 0.00–1.00 to 1.00. Pure titanium dioxide and zinc oxide as reference materials were also tested.

3.1. Hydrogen

Hydrogen itself is a desired product of the photochemical decomposition of water. It is also an intermediate product necessary for the photochemical decomposition of CO_2 into other valuable compounds. When irradiated with UV–Vis radiation, it is formed in the process of water splitting. Fig. 6 shows the graphs of the increase in the amount of hydrogen during the process for a group of materials containing TiO_2.

The amount of hydrogen generated after 6 h of the process was in the range of 4.1–19.2 $\mu mol/g_{material}/dm^3$. The highest value was observed for the 0.05 CS/TiO_2 sample and the lowest for the 0.50 CS/TiO_2 material. Only one of the five tested mixtures was characterized by higher hydrogen production activity compared to pure TiO_2, and that was the 0.05 CS/TiO_2 sample. In addition, hydrogen could not be detected for most samples until the second hour of the process. The graph shows fluctuations in the content of this component and even a decrease in its amount (e.g. for the sample 1.00 CS/TiO_2 – from 10.4 $\mu mol/g_{material}/dm^3$ after 4 h of the process to 7.8 $\mu mol/g_{material}/dm^3$ after 6 h). This can be explained by the fact that hydrogen in the CO_2 reduction process is an intermediate product continuously consumed in the reactions to form CO and CH_4.

No correlation was observed between the addition of carbon spheres and the amount of hydrogen produced. It can only be said that a small addition of carbon spheres (0.05 g of CS per 1 g of TiO_2) improved the photocatalytic properties of TiO_2 for hydrogen production. However, the further addition of carbon spheres negatively impacted the amount of H_2 produced.

Fig. 7 shows analogous diagrams for hydrogen production with ZnO as the active phase. In this case, slightly less hydrogen was obtained. It was in the range of 2.8–14.0 $\mu mol/g_{material}/dm^3$. In contrast to CS/TiO_2, the highest result was obtained for the sample with the highest addition of carbon spheres – 1.00 CS/ZnO, and at the same time it was the only material whose use resulted in the production of hydrogen at a level close to that of pure ZnO. In addition, a more significant effect of adding carbon spheres on H_2 production can be observed here. The hydrogen content decreased significantly at low CS additions, and it began to increase at the addition of $\geq$ 0.25 g of CS per 1 g of ZnO. Variations in the
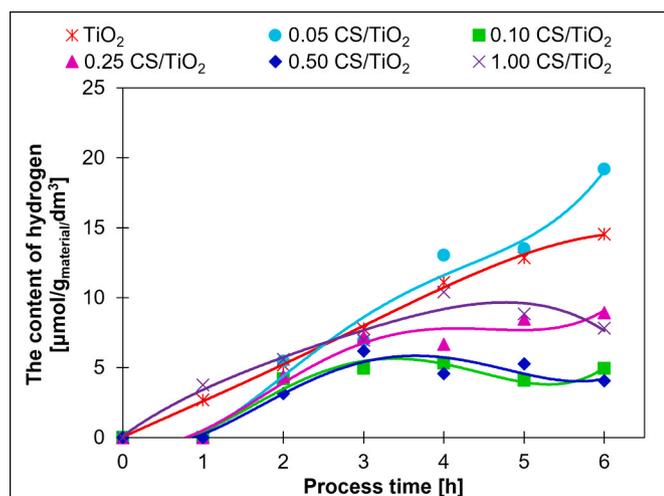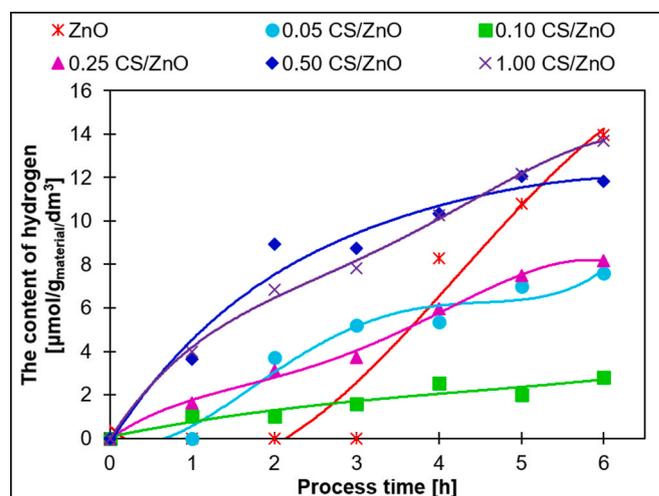
Fig. 7. The total content of H_2 in the gas phase after 6 h of the process with various CS/ZnO photocatalysts.

amount of this component can also be observed during the process. It is important to note that small amounts of hydrogen could already be detected after 1 h of the process in the tests with materials containing carbon spheres. At the same time, with pure ZnO it was visible on the chromatogram only after 4 h. Thus, it can be said that the addition of carbon spheres accelerates the process of hydrogen generation, but does not increase its amount.

Comparing the two groups of tested materials, it can be concluded that the amounts of hydrogen obtained were in a similar range, regardless of the active phase used. The addition of carbon spheres did not improve the photocatalytic properties of the materials for hydrogen production. Nevertheless, more favorable results were obtained for TiO_2 at a deficient CS concentration in the sample. On the other hand, for the ZnO samples, the highest amount of hydrogen was observed using the material with the highest percentage of carbon spheres tested.

A graph comparing the H_2 production after 6 h as a function of the number of carbon spheres for both tested groups is presented in Fig. 8. As mentioned earlier, in the presence of carbon dioxide, the hydrogen produced is consumed by producing carbon monoxide and methane. Therefore, photocatalysts used for a photocatalytic reduction of CO_2 should not be evaluated based on the amount of hydrogen produced.

3.2. Carbon monoxide

Carbon monoxide can be produced directly during the carbon

Fig. 6. The total content of H_2 in the gas phase after 6 h of the process with various CS/TiO_2 photocatalysts.
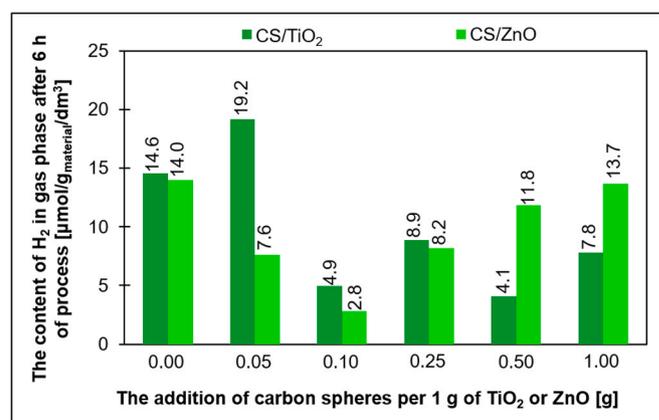
Fig. 8. The dependence of the amount of hydrogen after 6 h of process on the addition of carbon spheres for CS/TiO_2 and CS/ZnO materials.

dioxide reduction according to the reaction (3). At the same time, it can be a product of methane oxidation in reactions that take place under UV radiation [70]:

$$2CH_4 + 2O_2 \rightarrow 2CO + 4H_2O \tag{5}$$

$$2CH_4 + O_2 \rightarrow 2CO + 4H_2 \tag{6}$$

Under the conditions used in the experiments described in Section 2.5., carbon monoxide is the main product of the process. The graphs of the CO content in the gas phase for the subsequent CS/TiO_2 are shown in Fig. 9. It can be concluded that the addition of carbon spheres positively affected the production of carbon monoxide. For all tested mixtures of titanium dioxide with carbon spheres, the produced volumes of carbon monoxide were higher compared to pure TiO_2. The highest CO volume was obtained using 0.10 CS/TiO_2 material, and it was 19.3 $\mu mol/g_{material}/dm^3$ after 6 h of the process. Further additions of carbon spheres caused a decrease of carbon monoxide content in the gas phase to 11.5 $\mu mol/g_{material}/dm^3$ after 6 h of the process for the material with the highest CS addition (1.00 CS/TiO_2). For pure TiO_2, it was only 10.7 $\mu mol/g_{material}/dm^3$. It is also important to note that the amount of carbon monoxide increased linearly at different rates for all processes. The presence of CO in the gas phase was observed already after 1 h of the process. This fact allows us to conclude that the reduction of CO_2 began immediately after the irradiation started, and the addition of carbon spheres additionally accelerated this process, as evidenced by the higher amounts of CO obtained in tests with CS/TiO_2 mixtures.

In the case of materials containing ZnO, the amounts of obtained CO were in the range of 7.0–15.9 $\mu mol/g_{material}/dm^3$, as presented in Fig. 10. The highest result was noted for pure ZnO. Unlike for TiO_2, the addition of carbon spheres did not improve the photocatalytic properties of zinc oxide. It is interesting, however, that with the addition of carbon spheres between 0.05 and 0.25 g of CS per 1 g of ZnO, the carbon monoxide content decreased and then increased at higher CS contents in the samples. The highest result among the CS/ZnO mixtures was recorded for 1.00 CS/ZnO material, and it was 13.3 $\mu mol/g_{material}/dm^3$ after 6 h of process. Based on the results, it can be concluded that a higher addition of CS to ZnO is more advantageous, but it generally reduces the photoactivity of zinc oxide.

Comparing both groups of tested materials (Fig. 11), it can be assumed that similar amounts of carbon monoxide were produced in performed processes, although the tests using TiO_2–containing materials yielded slightly higher results. The most preferred amount of carbon spheres to TiO_2 was 0.10 g per 1 g of TiO_2. In turn, for ZnO, it was 1.00 g of CS per 1 g. However, it should be noted that despite that fact, a lower
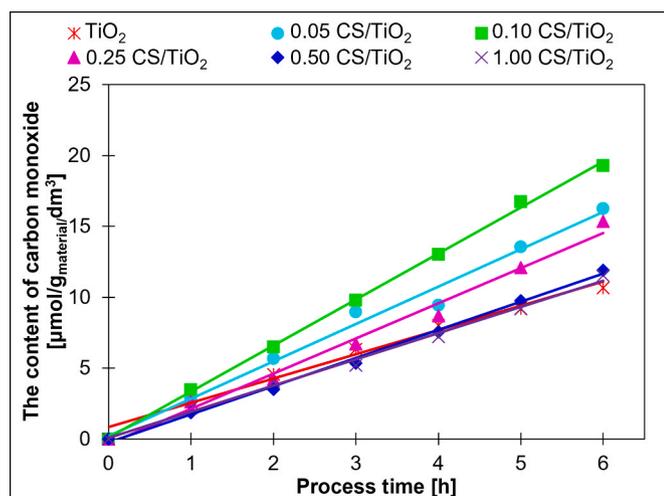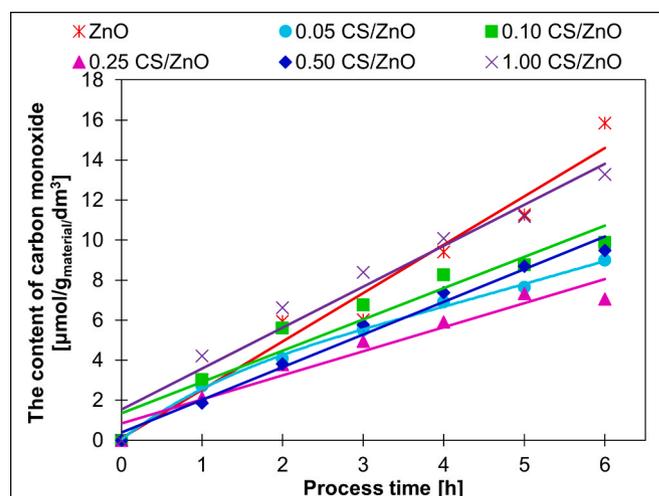
Fig. 10. The total content of CO in the gas phase after 6 h of the process with various CS/ZnO photocatalysts.
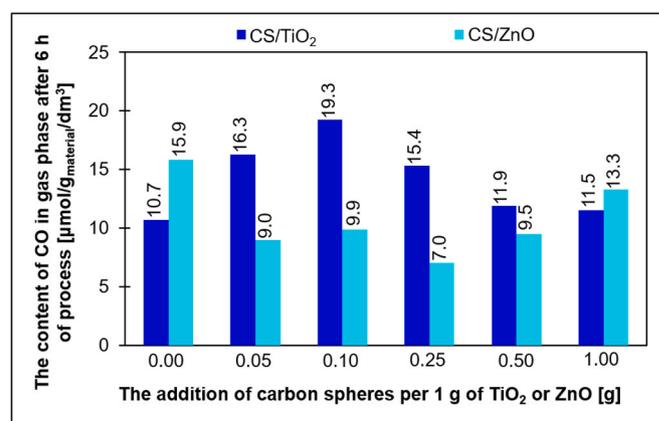
Fig. 11. The dependence of the amount of carbon monoxide after 6 h of process on the addition of carbon spheres for CS/TiO_2 and CS/ZnO materials.

result was obtained for this material compared to pure ZnO.

3.3. Methane

Methane is the last of the analysed products of the photocatalytic reduction of carbon dioxide. The production of this compound requires 8 electrons (Eq. (4)), which is why this reaction is the most difficult to perform. The energy and electrons present in the reactor are constantly involved in competing reactions. Additionally, methane molecules may undergo oxidation, as mentioned in Section 3.2.

In processes using CS/TiO_2 materials, small amounts of methane were obtained (0.4–0.6 $\mu mol/g_{material}/dm^3$), as presented in Fig. 12. Moreover, no correlation was revealed between the amount of produced CH_4 and the number of carbon spheres in the samples. Regardless of this, similar values of this compound were obtained.

Conclusions may be slightly different in the case of materials containing ZnO. Although the amounts of methane produced were also negligible, adding 1.00 g of CS to 1 g of ZnO increased methane production to 1.7 $\mu mol/g_{material}/dm^3$. For pure ZnO, it was only 0.5 $\mu mol/g_{material}/dm^3$. The summary graph for the group of CS/ZnO materials is shown in Fig. 13. Fig. 14 compares the amount of methane obtained after 6 h of the process for both groups of materials.

Fig. 9. The total content of CO in the gas phase after 6 h of the process with various CS/TiO$_2$ photocatalysts.
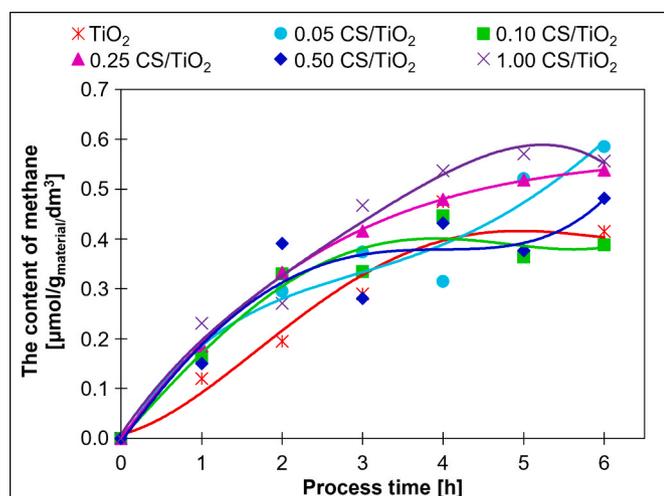
Fig. 12. The total content of CH_4 in the gas phase after 6 h of the process with various CS/TiO_2 photocatalysts.
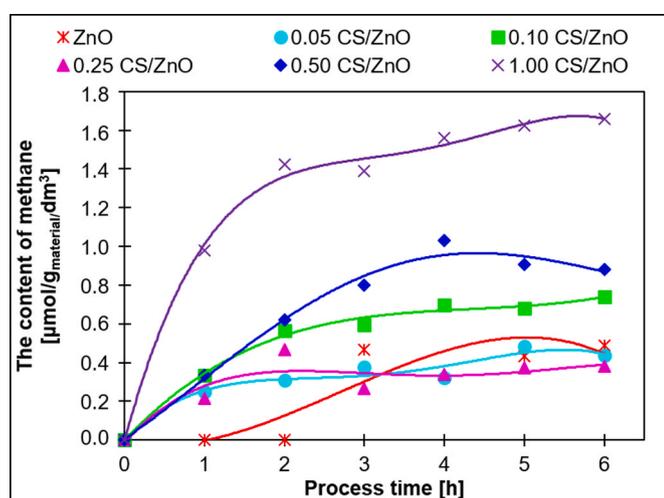
Fig. 13. The total content of CH_4 in the gas phase after 6 h of the process with various CS/ZnO photocatalysts.
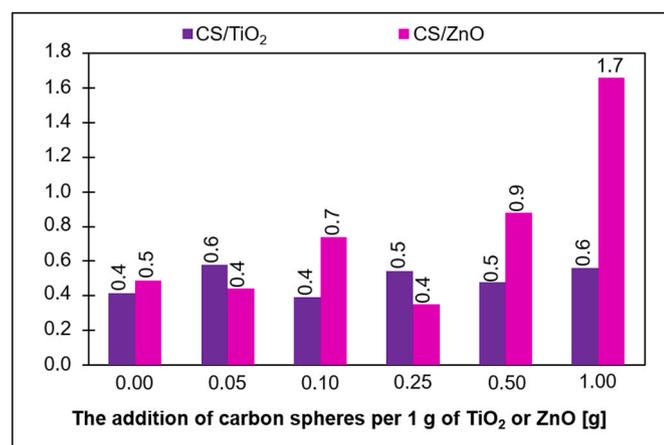
Fig. 14. The dependence of the amount of methane after 6 h of process on the addition of carbon spheres for CS/TiO_2 and CS/ZnO materials.

4. Conclusions

The experiments were carried out to evaluate the photocatalytic activity of two groups of materials containing TiO_2 and ZnO with the addition of carbon spheres in the amount of 0.05–1.00 g of CS per 1 g of TiO_2/ZnO in CO_2 reduction. These processes were performed in the liquid phase using 0.2 M NaOH aqueous solution. The samples were irradiated with UV–Vis light for 6 h.

Hydrogen, carbon monoxide, and methane products have been identified in the gas phase. The results were compared with those for initial materials, i.e. pure TiO_2 and ZnO. Based on the results, it can be concluded that both groups of materials generated similar amounts of the products mentioned above. However, samples containing TiO_2 had slightly higher activity in hydrogen and carbon monoxide production than ZnO–containing materials. On the other hand, more methane was produced in the processes using CS/ZnO samples, although it was an insignificant amount for all the tested samples.

The main product of the performed processes was carbon monoxide. Similar amounts of hydrogen were also obtained, although, in the reduction of CO_2, it was an intermediate product, constantly consumed in the reactions leading to the formation of CO and CH_4. It can also be assumed that adding carbon spheres to titanium dioxide improved its photocatalytic properties in the production of carbon monoxide. In the case of CS/ZnO materials, no increase in activity was observed.

Based on the results, it can be concluded that a smaller amount of carbon spheres was more efficient for TiO_2–containing materials (0.10 g of CS per 1 g of P25), while for ZnO, better results were obtained with the sample containing the most significant amount of carbon spheres (1.00 g of CS per 1 g of ZnO). This discrepancy may indicate that intermolecular interactions occurring in the materials may have a greater influence on the CO_2 photoreduction process than the pore size distribution or increased CO_2 adsorption capacity. The less negative zeta potential of ZnO resulted in closer contact with the carbon sphere particles, giving better results for samples with a higher CS content. In turn, the higher activity of TiO_2 compared to ZnO could result from its higher S_{BET} and TPV values. Due to this fact, the contact time between the photocatalyst and the CO_2 molecule was longer. On the other hand, improved adsorption capacity provided by carbon spheres addition can at some point positively affect the photocatalyst performance. It should be noted that this will also depend on the photocatalytic ability of the active material itself.

CRediT authorship contribution statement

Antoni W. Morawski: Conceptualization, Methodology, Writing – original draft, Writing – review & editing, Supervision. **Katarzyna Ćmielewska**: Formal analysis, Investigation, Writing – original draft, Writing – review & editing, Visualization. **Ewelina Kusiak-Nejman**: Conceptualization, Methodology, Writing – review & editing, Supervision. **Piotr Staciwa**: Formal analysis, Investigation, Visualization. **Joanna Kapica-Kozar:** Formal analysis, Investigation. **Ewa Ekiert**: Formal analysis, Investigation. **Iwona Pełech**: Conceptualization, Methodology, Writing – review & editing, Supervision. **Urszula Narkiewicz**: Supervision, Funding acquisition.

Declaration of Competing Interest

Data availability

No data was used for the research described in the article.

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