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Photocatalytic CO oxidation with water over Pt/TiO$_2$ catalysts

Krzysztof Czupryn[1] · Ireneusz Kocemba[1] · Jacek Rynkowski[1]

Abstract This paper reports that Pt/TiO$_2$ and to some extent, Pt/Al$_2$O$_3$ and Pt/SiO$_2$ catalysts show some activity in the photocatalytic oxidation of CO by water at low temperature (< 100 °C) in the absence of oxygen. For Pt/TiO$_2$ catalysts, CO conversion is dependent on the Pt loading as well as the temperature of their reduction. There are an optimal platinum loading (5 wt%) and catalyst reduction temperature (500 °C) ensuring the best photocatalytic efficiency. Catalytic performance results from the combined effects of electron–hole photogeneration and partial photodesorption of CO from the platinum surface, followed by the adsorption and subsequent dissociation of H$_2$O. The probable mechanism of photooxidation of CO by H$_2$O was proposed.

Keywords CO photooxidation · Water gas shift reaction · WGSR · Photocatalysis

Introduction

Catalytic CO oxidation by oxygen is an important reaction for the removal of air pollution. CO abatement is necessary because this extremely toxic, color-, odor- and tasteless gas presents a mortal threat to human and animal health. The catalytic oxidation of CO has been studied on numerous both metallic and oxide catalysts over the years [1–7]. The mixture of copper and manganese oxides (hopcalite) or gold deposited on some metal oxides exhibits very high activity towards the low-temperature oxidation of CO [8, 9].

It is worth mentioning that despite the toxicity of CO for multicellular organisms, some bacteria use it as a source of energy. Carbon monoxide oxidation depends on a

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molybdenum—containing enzyme, the aerobic CO dehydrogenase (CODH) [10]. The mentioned bacteria oxidize CO anaerobically by water.

On the other hand, catalytic CO oxidation by H_2O is an important reaction in industry for hydrogen production according to the following equation [11]:

$$CO + H_2O \rightarrow H_2 + CO_2 \ \Delta H_{298}^0 = -41.09 \ kJ/mol \tag{1}$$
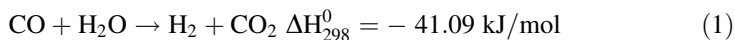
This reaction, called the water gas shift reaction (WGSR), is exothermic and reversible. The kinetics and the thermodynamics are in conflict. At the high temperature, the state of thermodynamic equilibrium is achieved faster, but low temperatures are conducive to achieving higher performance. Due to these restrictions, on an industrial scale WGSR is carried out in two stages: i/a high and ii/a low temperature shift reaction. The pressures occurring in the current industrial applications restrict the minimum of the low temperature shift with the use of classical $Cu–ZnO–Al_2O_3$ catalysts to about 250 °C. In the last two decades, there has been a growing interest in hydrogen fuel cell technologies. They use hydrogen generated most often by hydrocarbon reforming processes contaminated with CO. Unfortunately, even a trace content of CO in hydrogen (ppm level) leads to the poisoning of fuel cell electrodes. To avoid it, several hydrogen processing steps, including the removal of CO (more effective low temperature WGSR, preferential CO oxidation in the presence of hydrogen (PROX) must be developed. So far, the most promising catalytic systems for low temperature WGSR include Pt or Au catalysts supported on reducible oxides, mainly CeO_2, TiO_2 [3, 4] and very recently molybdenum carbides [5].

The photocatalytic oxidation of CO can be one of the alternative methods of carbon monoxide neutralization. The advantage of this method is that it can be effective at very low temperature (less than 100 °C) and may be used simultaneously towards various air pollutants such as volatile organic compounds (VOCs). The catalysts most commonly studied in photocatalytic processes contain titanium dioxide [12, 13]. The photocatalytic properties of TiO_2 are often modified by doping with another semi-conductive oxide or deposition of the metal phase on the surface. Pt/TiO_2 systems are very important and active photocatalysts in a number of different reactions [14–17]. The process of photocatalytic oxidation of carbon monoxide over Pt/TiO_2 is relatively widely described in literature [18–20]. Pt/TiO_2 systems, especially alkali promoted, are also considered promising catalysts in low temperature WGSR [8, 9].

Thus, it seemed interesting to search for the photocatalytic process of CO oxidation over Pt/TiO_2 catalysts in the oxygen free atmosphere using H_2O as an oxidant. To the best of our knowledge, such process has not been described yet.

An important aspect of this work can be an assessment of using of Pt/TiO_2 catalysts in photocatalytic CO oxidation by H_2O to purify the stream of neutral gases from CO.

Experimental

Catalysts preparation

Catalysts were prepared by impregnation of commercial titanium dioxide (TiO_2, Degussa P25, $a_S = 50$ m^2 g^{-1}) with an appropriate amount of aqueous $H_2PtCl_6 \cdot H_2O$ (Aldrich) solution to obtain the nominal Pt loading of 0.2, 1, 2, 5 and 10 wt%. After 24 h, water was evaporated, the samples were dried at 110 °C for 12 h and finally calcined in air at 500 °C for 4 h. Next, the samples were subjected to reduction in the stream of hydrogen for 60 min at a selected temperature: 200, 300, 400, 500 or 600 °C.

For comparative purposes, platinum catalysts with the nominal Pt loading of 1 wt% supported on nonreducible oxides SiO_2 (MERC, $a_S = 375$ m^2 g^{-1}) and Al_2O_3 (Fluca, $a_S = 125$ m^2 g^{-1}) were also prepared in the same way as Pt/TiO_2 catalysts.

Methods

Temperature-programmed reduction (TPR) and chemisorption studies were carried out in the apparatus PEAK—4 described in detail in [21].

The adsorption capacity of the tested catalysts for CO was determined by the pulsed method. A catalyst sample of 0.2 g was pretreated in the hydrogen atmosphere at 200 °C for 60 min. Then the reactor was cooled down to room temperature and a flow of H_2 was replaced by nitrogen. After purging the sample, the pulses of 0.05 cm^3 CO were introduced on the reactor using a six-way valve. The amount of adsorbed CO was calculated from the sum of CO pulses consumed by the catalyst, using FUJI IR gas analyzer.

Based on CO chemisorption, the dispersion of platinum, defined as the ratio of the number of surface metal atoms (Pt_S) to their total number, was estimated. The stoichiometry Pt: CO was assumed 1: 1 according to the following equation:

$$Pt_s + CO_{(gas)} \rightarrow Pt - CO_{(ads)} \tag{2}$$
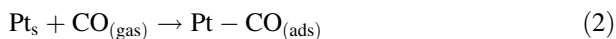
Before the H_2—TPR measurement, the sample of 0.2 g was annealed at 400 °C in the gas mixture containing 50 V% of O_2 in Ar for 1 h and then cooled down to room temperature. The reducing mixture (5 V% H_2 in Ar) flew through the catalyst bed at a volume rate of 40 cm^3 min^{-1} in the temperature range 25–800 °C with a linear increase of temperature 15 °C min^{-1}. Thermal conductivity detector (TCD) was used to monitor the changes of hydrogen concentration.

Photocatalytic test

The photocatalytic activity measurements were carried out in a hand-made, patented photoreactor [22] equipped with Perkin Elmer lamp PE-175B 10FM. The spectral distribution of this lamp shows that it is optimized for the visible range of radiation. The radiation with wavelengths < 400 nm constitutes only a few percent of the total one and it is practically limited to UVA. A full description of the light source is available in the datasheet on the website [23].

The reactor is shown in Fig. 1, while a diagram of the whole catalytic test equipment in Fig. 2.

The gaseous reaction mixture (0.5 V% CO in Ar) with a total flow rate 30 cm^3 min^{-1} was passed over a scrubber filled with deionized water and then fed to the reactor. The concentration of water vapor determined with the use of humidity sensors (HIH-4000-002, Honeywell) was ca. 2.5 V%.

The catalyst sample of 0.2 g was placed just below the quartz glass window (ϕ 50 mm) on a bed made of a glass fiber fabric with a diameter of 45 mm. The total flow rate and dimensions of the layer of the catalysts correspond to gas hourly space velocity (GHSV) 1122 h^{-1}. All the experiments were conducted at ambient temperature. After about 30 min of exposure to radiation, the temperature of the reactor increased to about 50 °C. Carbon dioxide as a product of CO oxidation was measured continuously in outlet gas stream using FUJI IR CO_2 analyzer. The maximum conversion of CO to CO_2 during a 30-min UV–VIS irradiation exposure time was used as a measure of catalytic activity. A conversion was calculated using the formula:

$$C_{CO} = \frac{c_1}{c_2} \times 100\% \tag{3}$$

Here c_1, c_2 are the concentrations of CO_2 in the reactor output and CO in the reactor input.

Results and discussion

Characterization of Pt/TiO$_2$ catalysts

Platinum dispersion

The results of CO chemisorption and Pt dispersion for Pt/TiO$_2$ catalysts reduced at different temperatures are summarized in Table 1.
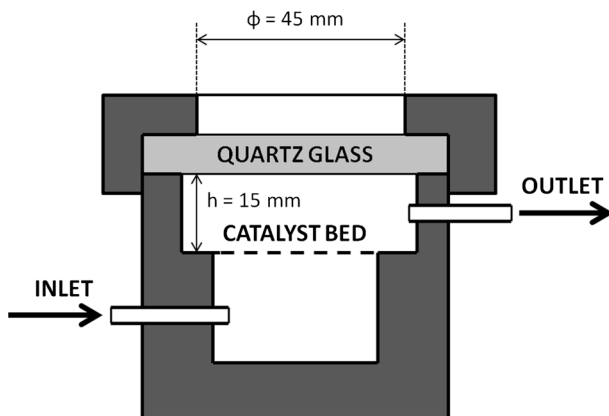

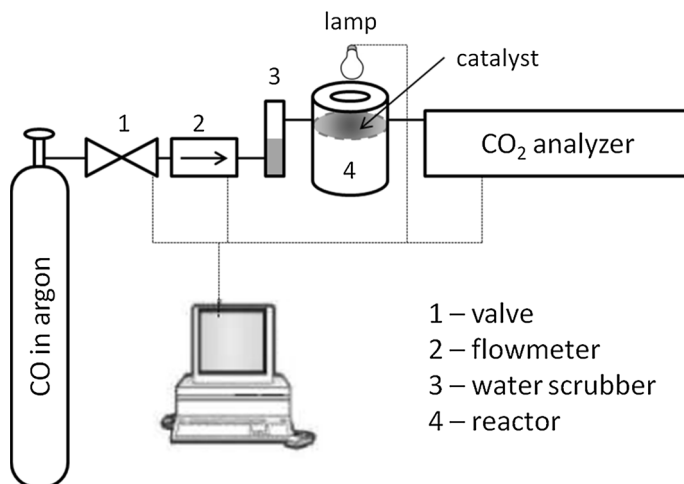**Fig. 1** Stainless steel reactor with quartz window

Fig. 2 Diagram of catalytic equipment used for photocatalytic activity measurements

The results presented in Table 1 indicate that the catalysts show increased CO adsorption capacity with the increase in the platinum content. On the other hand, a substantial decrease in the volume of adsorbed CO with an increasing reduction temperature was observed. For example, the volume of adsorbed CO by $10Pt/TiO_2$ catalyst after the reduction at 600 °C is nearly 70 times lower than after the reduction at 200 °C. The dispersion of platinum in the studied catalysts decreases with the increase in the reduction temperature. Basically, the dispersion decreases also with the increase in the platinum loading although some discrepancies can be observed connected probably with the adoption of simplifying assumptions of CO:Pt stoichiometry.

The catalyst $0.2Pt/TiO_2$ reduced at 200 °C shows the highest dispersion among the catalysts under study (21%) due to the small content of the metal phase, evenly distributed on the support surface, which prevents agglomeration of the platinum particles.

TPR analysis

Fig. 3 shows the H_2-TPR profiles of TiO_2 and Pt/TiO_2 samples. In the case of TiO_2, the reduction starts in fact at 330 °C and the broad hydrogen consumption peak with the maximum at ca. 670 °C is observed. It may be ascribed to the reduction of the surface oxygen, leading to the creation of oxygen vacancies on the TiO_2 surface [10]. The reduction of Pt/TiO_2 catalysts occurs in general in two temperature ranges. The first starts at ca. 60 °C (for the $10Pt/TiO_2$ catalyst already at ambient temperature) and can be associated with the reduction of PtO_x oxides. The higher the content of platinum in the catalyst, the more the maximum of low temperature peak is shifted towards higher temperature (from 100 °C for $10Pt/TiO_2$ to 170 °C for $0.2Pt/TiO_2$). The high temperature consumption of hydrogen starts at about 350 °C. For the catalysts $5Pt/TiO_2$ and $10Pt/TiO_2$, it continues up to 800 °C, the

Table 1 CO chemisorption and Pt dispersion for Pt/TiO$_2$ catalysts reduced at different temperatures

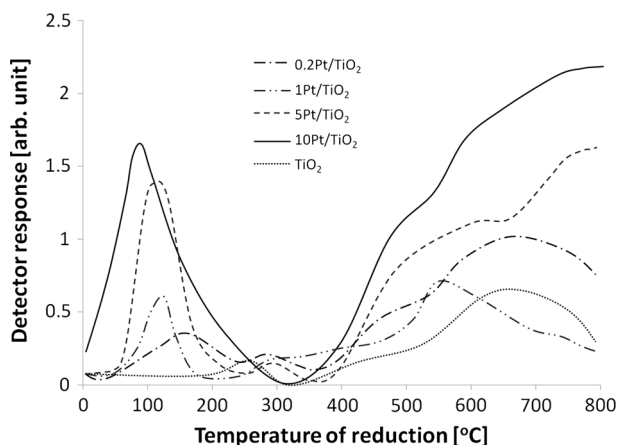| Catalyst	Volume of adsorbed CO (N cm^3 g$_{cat}$$^{-1}$)					Dispersion (%)				
Reduction temperature	200 °C	300 °C	400 °C	500 °C	600 °C	200 °C	300 °C	400 °C	500 °C	600 °C
0.2Pt/TiO$_2$	0.048	0.048	0.024	0.015	0.011	21.0	20.8	10.6	6.4	4.9
1Pt/TiO$_2$	0.053	0.032	0.025	0.023	0.006	4.7	2.8	2.2	2.0	0.5
2Pt/TiO$_2$	0.118	0.104	0.079	0.033	0.004	5.1	4.5	3.4	1.4	0.2
5Pt/TiO$_2$	0.428	0.279	0.117	0.033	0.013	7.5	4.9	2.0	0.6	0.2
10Pt/TiO$_2$	0.629	0.502	0.267	0.030	0.009	5.5	4.4	2.3	0.3	0.1

Fig. 3 H_2-TPR profiles of support TiO_2 and platinum catalysts Pt/TiO_2

final temperature of heating. The profiles of other catalysts show maxima and shoulders at different temperatures within the range 460–720 °C and reflect the presence of differently coordinated oxygen species on TiO_2 showing the disparate susceptibility to reduction [10, 11]. Moreover, the presence of Pt facilitates the reduction of TiO_2 due to the spillover of hydrogen [24]. To sum up, the reduction of catalysts at temperatures above 400 °C causes the formation of a non-stoichiometric form of titanium dioxide with anionic vacancies on the support surface. This phenomenon can affect the final photocatalytic activity of Pt/TiO_2 catalysts strongly. This problem will be widely discussed in next section.

The activity tests and overall discussion

The photocatalytic activity of the Pt/TiO_2 catalysts was evaluated for CO oxidation by H_2O. CO conversion vs. the temperature of $1Pt/TiO_2$ catalyst reduction is shown in Fig. 4. The maximum conversion (16.6%) is reached for the catalyst reduced at 500 °C. Such a result shows that there is an optimal reduction temperature which allows obtaining the highest activity. The change of photocatalytic activity with the temperature of the catalyst reduction is not in line with that of platinum dispersion (Table 1). The platinum dispersion decreases gradually as the reduction temperature increases, whereas the catalyst activity reaches its maximum at 500 °C. If we notice that the intensive consumption of hydrogen takes place in the temperature range 470–550 °C (see the TPR profile of $1Pt/TiO_2$ catalyst), one can conclude that the presence of the non-stochiometric forms of titanium dioxide is necessary to display a reasonable photocatalytic activity. Taking this conclusion into account, the influence of Pt loading on the activity of Pt/TiO_2 catalysts reduced at 500 °C was studied. The results are presented in Fig. 5.

An increase in the platinum loading up to 5 wt% results in the increase in the catalyst photoactivity. However, a further rise in the platinum concentration does
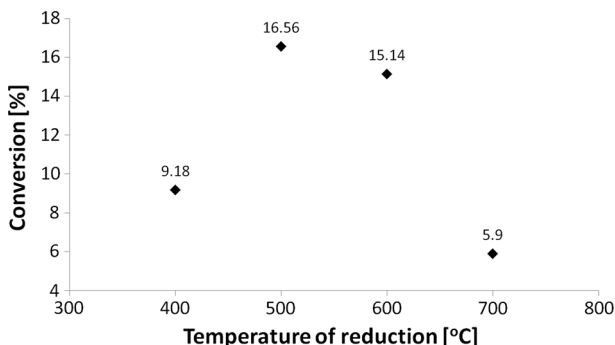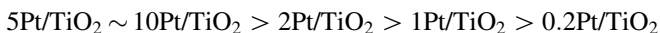
Fig. 4 The photocatalytic activity of $1Pt/TiO_2$ catalyst vs the temperature of its reduction

not increase it. Thus, all Pt/TiO_2 catalysts under study reduced at 500 °C can be specified in the order of decreasing activity as follows:

$$5Pt/TiO_2 \sim 10Pt/TiO_2 > 2Pt/TiO_2 > 1Pt/TiO_2 > 0.2Pt/TiO_2$$

In photocatalysis, besides the chemisorption properties, the photocatalytic activity depends on the ability of the catalyst to create electron–hole pairs generating free radicals able to undergo secondary reactions. In catalyzed photolysis, light is absorbed by an adsorbed substrate(s), so the bond cleavage is induced just by radiation [16, 25].

In order to distinguish which mechanism triggers activation of the studied reaction, the activity of the platinum deposited on the insulator oxides (Al_2O_3 and SiO_2) was investigated.

Fig. 6 shows CO conversion over $1Pt/TiO_2$, $1Pt/SiO_2$ and $1Pt/Al_2O_3$ catalysts. Both $1Pt/Al_2O_3$ and $1Pt/SiO_2$ catalyze CO oxidation to some extent. After 35 min of
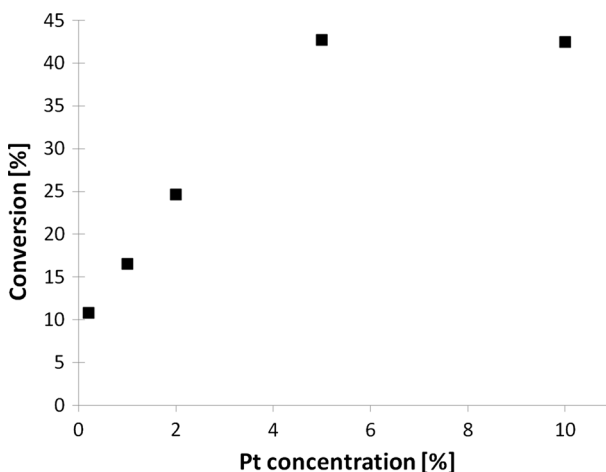

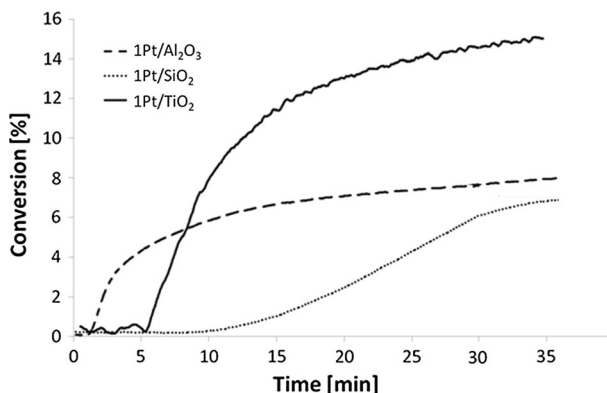**Fig. 5** The photocatalytic activity according to the concentration of Pt in a catalyst

Fig. 6 CO conversion over $1Pt/TiO_2$, $1Pt/SiO_2$ and $1Pt/Al_2O_3$ catalysts during a 35-min UV–VIS irradiation exposure

UV–VIS irradiation, conversions 6 and 8% were recorded for $1Pt/Al_2O_3$ and 1Pt/SiO_2, respectively. These values were approximately twice as low as that of 1Pt/TiO_2. Alumina and silica are characterized by a wide energy gap, which prevents transferring of the electron from the valence band to the conduction band [26]. Therefore, in the case of these supports, the CO oxidation with water can only take place by activating substrates adsorbed onto the surface of the catalysts. The process of activation could only be connected with water photodisociation.
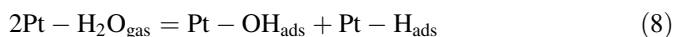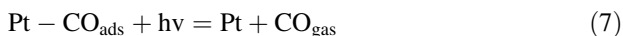
$$H_2O + hv \rightarrow H^* + OH^* \tag{4}$$

In the next step, the process of CO oxidation via hydroxyl groups would occur:

$$CO + OH^* \rightarrow CO_2 + H^* \tag{5}$$
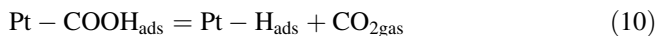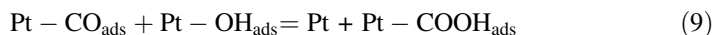
$$2H^* \rightarrow H_2 \tag{6}$$

However, if we take into account the spectral characteristic of the used UV–VIS lamp, reaction (4) is absolutely improbable. Only in the case of the high-energy photons ($\lambda < 125$ nm) the photogeneration of OH and H radicals as a result of water photolysis takes place [27].

Thus, it needs to be explained why CO oxidation over Pt/Al_2O_3 and Pt/SiO_2 catalysts occurs. It should be highlighted here that no conversion of CO over all (Pt/TiO_2, Pt/Al_2O_3 and Pt/SiO_2) catalysts under study is observed if the radiation is switched off. Obviously, CO conversion must be induced by UV–VIS irradiation, but the role of light is different than in the photocatalytic or photolytic processes. We anticipate that it is connected with platinum affinity to CO adsorption. It was proved that carbon monoxide binds very strongly to the Pt surface and adsorption of CO on the metallic Pt surface can very effectively block adsorption of other gases. Thus, CO may be considered a poison for the platinum catalyst. This phenomenon plays a very negative role in some catalytic processes, for example in NO_x reduction with H_2 or in anodic hydrogen oxidation in proton exchange membrane fuel cells (PEM) [28–30]. Thus, the platinum surface can be completely poisoned by CO and

in this state there are no free adsorption centers. It was mentioned earlier that the reaction between CO and H_2O demands water dissociation. The phenomenon of water adsorption and its dissociation over platinum catalysts is described in literature [31]. Recently, water dissociation on five platinum surfaces, i.e. Pt(111) Pt(100), Pt(110), Pt(211), and Pt(321) has been investigated [32]. It was found that water molecules adsorb more strongly on surfaces presenting low coordinated atoms. The effect of the Pt particle size on the adsorption and dissociation energies of the water molecule was investigated using DFT by the authors of work [33]. These examples demonstrate that the process of H_2O adsorption and dissociation over a platinum surface of the investigated catalysts is possible. Under the conditions at which the process is realized without radiation, the surface of platinum is completely covered by carbon monoxide. Switching on the light radiation leads to partial desorption of CO, allowing adsorption and dissociation of H_2O. This process can be described by reactions:

$$Pt - CO_{ads} + hv = Pt + CO_{gas} \tag{7}$$

$$2Pt - H_2O_{gas} = Pt - OH_{ads} + Pt - H_{ads} \tag{8}$$

As a result, the reaction of CO oxidation begins to run according to the reactions:

$$Pt - CO_{ads} + Pt - OH_{ads} = Pt + Pt - COOH_{ads} \tag{9}$$

$$Pt - COOH_{ads} = Pt - H_{ads} + CO_{2gas} \tag{10}$$

The above considerations assume that the light radiation used in this work can cause carbon monoxide desorption from the platinum surface. To check it, the following experiment was conducted: prior to the desorption run, the sample was saturated with CO from the gas mixture 0.5 CO V% in Ar for 30 min at room temperature. Next, a flowing gas mixture was replaced by argon and light radiation was switched on. In the outlet gas stream, the concentration of CO was measured using Infrared Fuji Gas Analyser type ZRJ-4 (detection limits: 0.1 ppm). Fig. 7 shows the results for 1Pt/Al_2O_3, 1Pt/SiO_2 and 1Pt/TiO_2 samples. The process of CO desorption occurs for all catalysts. The shape of profiles is similar and the amount of CO desorbed changes in the order: 1Pt/TiO_2 ∼ 1Pt/Al_2O_3 > 1Pt/SiO_2. The area of peaks, which reflects the volume of desorbed CO, is the highest for 1Pt/Al_2O_3 sample and the lowest for 1Pt/SiO_2. It is understandable because these samples show the highest and the lowest sorption capacity to CO.

It is also worth noting that carbon monoxide starts to desorb in the same order as CO conversion begins (Fig. 6). To summarize, one can conclude that under light radiation CO desorbs from the platinum surface. This phenomenon allows water adsorption followed by its dissociation and the creation of hydroxyl groups. However, the problem remains whether at room temperature these hydroxyl groups can react with carbon monoxide [reaction (9)]. To check it, the following test was conducted. The gas mixture 2.5 V% H_2O in argon was passed through the reactor with a catalyst sample directly after its reduction. Next, the flow of H_2O/Ar was replaced by the mixture 0.5 CO V% in argon and the concentration of CO_2 in the
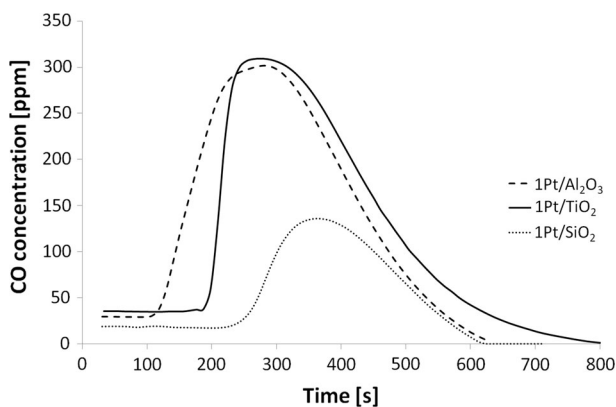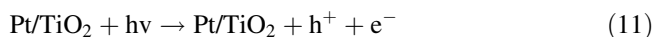
Fig. 7 CO desorption for 1Pt/TiO$_2$, 1Pt/SiO$_2$ and 1Pt/Al$_2$O$_3$ catalysts resulting from UV–VIS irradiation exposure

outlet gas stream was measured. The presence of carbon dioxide in the stream of gas mixture will prove that chemical reactions described by Eqs. (9) and (10) occur. This experiment revealed that WGS reaction can occur over a platinum catalyst already at room temperature. Without light irradiation, this reaction is not observed at low temperature due to the total covering of the platinum surface by carbon monoxide and the lack of adsorption sites for H$_2$O. Thus, it can be assumed that water dissociation is the rate determining step in the WGS reaction catalyzed by platinum at low temperatures. The effective catalysts operating at low temperatures should provide adsorption sites for both CO and H$_2$O. The authors of work [34] report that their platinum catalyst can effectively oxidise CO by H$_2$O at just low temperatures. Their results show that the surface Pt-OHx species are stabilized by alkali ions (sodium or potassium). The alkali ion associated surface OH groups are activated by CO and partially oxidized Pt-alkali-O(x)(OH)(y) species are the active sites for the low-temperature Pt-catalyzed WGS reaction.

In the case of the photocatalytic WGSR over platinum catalysts, the active sites for H$_2$O adsorption are created after switching on the light radiation. These carbon monoxide molecules, which are more weakly bound to the platinum surface, desorb creating sites for water adsorption. This step in the photocatalytic WGS reaction is the same for all platinum catalysts independently of the kind of support (insulator or semiconductor oxides). In the next step, in the case of Pt/Al$_2$O$_3$ and Pt/SiO$_2$ catalysts, light radiation only maintains the presence of adsorption sites for water adsorption. The total CO conversion is rather small and stays at an average level of only a few percent (Fig. 6). In the case of Pt/TiO$_2$ catalysts, the light radiation plays a double role. The first is the same as in the case of Pt/Al$_2$O$_3$ and Pt/SiO$_2$ catalysts, that is the creation and maintenance of the presence of adsorption sites for water adsorption. The second is connected with the creation of hole-electron pairs.

$$\text{Pt/TiO}_2 + h\nu \rightarrow \text{Pt/TiO}_2 + h^+ + e^- \tag{11}$$

This reaction describes the well known process of photocatalyst activation by the ultraviolet radiation. The electron and the hole can react with the molecules adsorbed on the catalyst surface. In the case of the photocatalytic WGS reaction, the hole can react with adsorbed water molecules to produce free radicals (OH) which show high reactivity and react with carbon monoxide creating a carboxyl group. Their disintegration leads to the formation of carbon dioxide and hydrogen.

$$H_2O + h^+ \rightarrow HO + H^+ \tag{12}$$

$$2H^+ + 2e^- \rightarrow H_2 \tag{13}$$

$$OH + CO \rightarrow COOH \tag{14}$$

$$2COOH \rightarrow 2CO_2 + H_2 \tag{15}$$

It is worth noting that this mechanism is practically the same as the one given by reactions (7)–(10). The difference lies only in the origin of hydroxyl groups and their concentrations. In the first case, they are created by H_2O dissociation on the platinum surface and their concentration is very low, in the second, these groups are mainly created as the effect of interaction of TiO_2 with UV radiation and their concentration is higher. Obviously, the higher concentration of OH groups leads to the increase in CO conversion.

Another issue is the process of creation of hole–electron pairs over Pt/TiO_2 catalysts. The energy gap of TiO_2 is 3.2 eV (anatase), which allows the electron to be transferred from the valence band to the conduction band under UV [35]. It was earlier mentioned that in the case of the light used in this work, UV constitutes only a few percent of the total radiation. This means that the efficiency of reaction (11) is low. On the other hand, the energy gap of TiO_2 strongly depends on its chemical state. The reduction of Pt/TiO_2 catalysts leads not only to the reduction of platinum oxides but also, to some extent, to the surface reduction of TiO_2. As it was shown in Fig. 3, the presence of Pt facilitates the reduction of TiO_2, which can be described by the general equation

$$TiO_2 + xH_2 \rightarrow TiO_{2-x} + xH_2O \tag{16}$$

Or

$$H_{2(gas)} + O_{o^x} \rightarrow H_2O + V_{o^*} \tag{17}$$
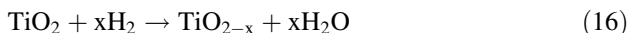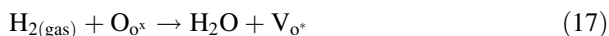
The second reaction refers to the formation of the surface vacancy (Vo*) linked with the reduction of TiO_2.

The creation of anionic vacancies can cause the reduction of the energy gap between the conduction band and the valence band of the titanium dioxide. This phenomenon strongly affects the final photocatalytic activity of Pt/TiO_2 catalysts. Thus, it can be assumed that the reduction of the band gap of TiO_2 increases the sensitivity of Pt/TiO_2 catalysts to visible light. From this point of view, the increase in TiO_2 reduction should be desirable. On the other hand, the results presented in Fig. 3 indicate that there is an optimal catalyst reduction temperature ensuring the

best activity of Pt/TiO$_2$ catalysts. In our opinion, at this temperature on the one hand, the sufficient modification of the energy gap of TiO$_2$ is reached, on the other, one platinum is completely reduced and shows relatively high sorption capacity to CO. After reduction at temperatures higher than 500 °C, CO adsorption was very low (Table 1). It is also worth noting that the reduction at a high temperature can lead to the formation of strong metal-support interactions (SMSI)—the phenomenon well known and repeatedly reported [36–38]. SMSI occurs in the catalysts supported on easily or moderately reducible oxides and causes a decrease in the CO sorption capacity of the catalysts. Pt/TiO$_2$ catalysts are one of the most prone to SMSI. It must also be remembered that platinum in the Pt/TiO$_2$ photocatalyst not only provides catalytic sites, but also traps photogenerated electrons. In this manner, platinum prevents electron–hole recombination, leading to a higher photocatalytic activity of titanium dioxide. Thus, the optimal concentration of platinum on the TiO$_2$ surface and the optimal reduction temperature result from all the factors which determine the role of platinum in Pt/TiO$_2$ photocatalysts. Some of these factors are still unknown.

Conclusions

Supported platinum catalysts (mainly Pt/TiO$_2$ but to some extent also Pt/Al$_2$O$_3$ and Pt/SiO$_2$) show some activity in the photocatalytic oxidation of CO by water at temperature less than 100 °C in the absence of oxygen. The activity of the catalysts supported on insular oxides is connected with the photodesorption of CO from the platinum surface, allowing the adsorption and subsequent dissociation of H$_2$O. In the case of Pt/TiO$_2$ catalysts, their higher activity results from the combined effects of electron–hole photogeneration and partial photodesorption of CO from the platinum surface. There are an optimal platinum loading (5 wt%) and catalyst reduction temperature (500 °C) ensuring the best photocatalytic efficiency of the catalysts under study.

References

1. Gubán D, Tompos A, Bakos I et al (2017) CO oxidation and oxygen reduction activity of bimetallic Sn–Pt electrocatalysts on carbon: effect of the microstructure and the exclusive formation of the Pt3Sn alloy. Reac Kinet Mech Cat 121(1):43–67. https://doi.org/10.1007/s11144-017-1152-8
2. Ratnasamy C, Wagner J (2009) Water gas shift catalysis. Cat Rev 51(3):325–440. https://doi.org/10.1080/01614940903048661
3. Centeno MA, Reina TR, Ivanova S et al (2016) Au/CeO$_2$ catalysts: structure and CO oxidation activity. Catalysts. https://doi.org/10.3390/catal6100158

4. Fu Q, Saltsburg H, Flytzani-Stephanopoulos M (2003) Active nonmetallic Au and Pt species on ceria-based water-gas shift catalysts. Science 301(5635):935–938. https://doi.org/10.1126/science.1085721

5. Yao S, Zhang X, Zhou W et al (2017) Atomic-layered Au clusters on α-MoC as catalysts for the low-temperature water-gas shift reaction. Science. https://doi.org/10.1126/science.aah4321

6. King GM, Weber CF (2007) Distribution, diversity and ecology of aerobic CO-oxidizing bacteria. Nat Rev Microbiol 5(2):107–118. https://doi.org/10.1038/nrmicro1595

7. Chotigkrai N, Hochin Y, Panpranot J et al (2016) Tuning Pt dispersion and oxygen mobility of Pt/γ-Al$_2$O$_3$ by Si addition for CO oxidation. Reac Kinet Mech Cat 117(2):565–581. https://doi.org/10.1007/s11144-015-0969-2

8. Panagiotopoulou P, Kondarides DI (2009) Effects of alkali promotion of TiO$_2$ on the chemisorptive properties and water-gas shift activity of supported noble metal catalysts. J Catal 267(1):57–66. https://doi.org/10.1016/j.jcat.2009.07.014

9. Zhu X, Hoang T, Lobban LL et al (2009) Significant improvement in activity and stability of Pt/TiO$_2$ catalyst for water gas shift reaction via controlling the amount of Na addition. Catal Lett 129(1–2):135–141. https://doi.org/10.1007/s10562-008-9799-4

10. Amano F, Nakata M (2014) High-temperature calcination and hydrogen reduction of rutile TiO$_2$: a method to improve the photocatalytic activity for water oxidation. Appl Catal B 158–159:202–208. https://doi.org/10.1016/j.apcatb.2014.04.025

11. Bouzoubaa A, Markovits A, Calatayud M et al (2005) Comparison of the reduction of metal oxide surfaces: TiO$_2$-anatase, TiO$_2$-rutile and SnO$_2$-rutile. Surf Sci 583(1):107–117. https://doi.org/10.1016/j.susc.2005.03.029

12. Callaghan C, Fishtik I, Datta R et al (2003) An improved microkinetic model for the water gas shift reaction on copper. Surf Sci 541(1–3):21–30. https://doi.org/10.1016/S0039-6028(03)00953-1

13. Rase HF (1977) Chemical reactor design for process plants. Wiley, New York

14. Bard AJ (1980) Photoelectrochemistry. Science 207(4427):139–144

15. Diebold U (2003) The surface science of titanium dioxide. Surf Sci Rep 48(5):53–229. https://doi.org/10.1016/S0167-5729(02)00100-0

16. Mills A, Le Hunte S (1997) An overview of semiconductor photocatalysis. J Photochem Photobiol A 108(1):1–35. https://doi.org/10.1016/S1010-6030(97)00118-4

17. Litter MI (1999) Heterogeneous photocatalysis transition metal ions in photocatalytic systems. Appl Catal B 23(2):89–114. https://doi.org/10.1016/S0926-3373(99)00069-7

18. Kolobov NS, Svintsitskiy DA, Kozlova EA et al (2017) UV-LED photocatalytic oxidation of carbon monoxide over TiO$_2$ supported with noble metal nanoparticles. Chem Eng J 314:600–611. https://doi.org/10.1016/j.cej.2016.12.018

19. Mohamed RM, Aazam ES (2011) Preparation and characterization of platinum doped porous titania nanoparticles for photocatalytic oxidation of carbon monoxide. J Alloy Compd 509(41):10132–10138. https://doi.org/10.1016/j.jallcom.2011.08.059

20. Li Q, Wang K, Zhang S et al (2006) Effect of photocatalytic activity of CO oxidation on Pt/TiO$_2$ by strong interaction between Pt and TiO$_2$ under oxidizing atmosphere. J Mol Catal A: Chem 258(1–2):83–88. https://doi.org/10.1016/j.molcata.2006.05.030

21. Kocemba I (2003) The PEAK-4 instrument for studying catalysts by temperature-programmed methods. Przem Chem 82(3):142–145

22. Kocemba I, Góralski J Reaktor przepływowy, zwłaszcza do prowadzenia fotokatalitycznych reakcji gazowych w funkcji temperatury(P390265)

23. http://pdf1.alldatasheet.com/datasheet-pdf/view/14926/PERKINELMER/PE175B-10F.html

24. Malevich DV, Masez AF, Matys VG et al (2001) Hydrogen spillover on supported TiO$_2$ films doped by platinum particles. In: Guerrero-Ruiz A, Rodríguez-Ramos I (eds) Spillover and Mobility of Species on solid surfaces, vol 138. Elsevier, Amsterdam, pp 101–108

25. Braslavsky SE (2007) Glossary of terms used in photochemistry, 3rd edition (IUPAC Recommendations 2006). Pure Appl Chem 79(3):293–465. https://doi.org/10.1351/pac200779030293

26. Robertson J (2006) High dielectric constant gate oxides for metal oxide Si transistors. Rep Prog Phys 69(2):327–396. https://doi.org/10.1088/0034-4885/69/2/R02

27. Robert WuC (2002) Extreme ultraviolet photon-induced chemical reactions in the C$_2$H$_2$–H$_2$O Mixed Ices at 10 K. Icarus 156(2):456–473. https://doi.org/10.1006/icar.2001.6801

28. Yu X, Wang Y, Kim A et al (2017) Observation of temperature-dependent kinetics for catalytic CO oxidation over TiO$_2$ -supported Pt catalysts. Chem Phys Lett 685:282–287. https://doi.org/10.1016/j.cplett.2017.07.078

29. He J, Shen Y, Yang M et al (2017) The effect of surface strain on the CO-poisoned surface of Pt electrode for hydrogen adsorption. J Catal 350:212–217. https://doi.org/10.1016/j.jcat.2017.04.004

30. Trens P, Durand R, Coq B et al (2009) Poisoning of Pt/C catalysts by CO and its consequences over the kinetics of hydrogen chemisorption. Appl Catal B 92(3–4):280–284. https://doi.org/10.1016/j.apcatb.2009.08.004

31. van der Niet MJTC, Garcia-Araez N, Hernández J et al (2013) Water dissociation on well-defined platinum surfaces: the electrochemical perspective. Catal Today 202:105–113. https://doi.org/10.1016/j.cattod.2012.04.059

32. Fajín JLC, DS Cordeiro MN, Gomes JRB (2014) Density functional theory study of the water dissociation on platinum surfaces: general trends. J Phys Chem A 118(31):5832–5840. https://doi.org/10.1021/jp411500j

33. Fajín JL, Bruix A, Cordeiro MN et al (2012) Density functional theory model study of size and structure effects on water dissociation by platinum nanoparticles. J Chem Phys. https://doi.org/10.1063/1.4733984

34. Zhai Y, Pierre D, Si R et al (2010) Alkali-stabilized Pt-OHx species catalyze low-temperature water-gas shift reactions. Science 329(5999):1633–1636. https://doi.org/10.1126/science.1192449

35. Nagaveni K, Hegde MS, Ravishankar N et al (2004) Synthesis and structure of nanocrystalline TiO_2 with lower band gap showing high photocatalytic activity. Langmuir 20(7):2900–2907. https://doi.org/10.1021/la035777v

36. Horsley JA (1979) A molecular orbital study of strong metal-support interaction between platinum and titanium dioxide. J Am Chem Soc 101(11):2870–2874

37. Dulub O, Hebenstreit W, Diebold U (2000) Imaging cluster surfaces with atomic resolution: the strong metal-support interaction state of Pt supported on TiO_2 (110). Phys Rev Lett 84(16):3646–3649

38. Tauster SJ, Fung SC (1978) Strong metal-support interactions: occurrence among the binary oxides of groups IIA–VB. J Catal 55(1):29–35. https://doi.org/10.1016/0021-9517(78)90182-3