Photocatalytic Reduction of CO₂ Over Me (Pt, Pd, Ni, Cu)/TiO₂ Catalysts

Oleksandr Shtyka^{1,2} · Radosław Ciesielski^{1,2} · Adam Kedziora^{1,2} · W. Maniukiewicz¹ · Sergey Dubkov² · Dmitry Gromov² · Tomasz Maniecki^{1,2}

Published online: 15 February 2020
© The Author(s) 2020

Abstract

A series of TiO₂ photocatalysts loaded with various metals (Pt, Pd, Ni, and Cu) were prepared by using the wet impregnation method. Their physicochemical properties were studied by using XRD, BET, TPR-H₂, FTIR and TPD-NH₃/CO₂ techniques. The photocatalytic activity of samples was investigated in the gas-phase reduction of carbon dioxide under continuous flow operation mode. Among all investigated catalysts, the Pt and Ni were the most active in terms of the formation rate of methanol. In general, the photocatalytic activity of modified TiO₂ decreased with increasing metal loading and reaction time. The reversible deactivation of photocatalysts was associated with the covering of TiO₂ surface by the reaction products.

Keywords Photocatalysis · CO₂ reduction · TiO₂ · Deactivation

1 Introduction

The photocatalytic conversion of carbon dioxide into value-added chemicals is recognized as a promising approach to address both energy and environmental issues. The process itself is similar to natural photosynthesis wherein CO₂ and H₂O are converted by plants to oxygen and carbohydrates. It basically consists of several steps which are [1]:

- absorption of photons and generation of electron–hole pairs;
- photoinduced charge recombination and transportation;
- oxidation of water caused by the hole in the valence band;
- reduction of CO₂ caused by the electron in the conduction band;

As a result, the carbon dioxide can be reduced to various chemicals, such as methane (CH₄), methanol (CH₃OH),

formic acid (HCOOH), carbon monoxide (CO), and others [2]. Among them, methanol is of prime interest due to its vast industrial use and applicability in the energy-related sector. For instance, it is widely used as a precursor for the synthesis of many industrial chemicals including formaldehyde, methyl *tert*-butyl ether, and acetic acid, which are used in adhesives, solvents, washer fluids, etc.

The photocatalytic reduction of carbon dioxide can be performed on various kinds of material, including inorganic semiconductors, carbon-based semiconductors, metal complexes, supermolecules, and their derivatives [3].

The key step in the photocatalytic process is the initial adsorption and activation of CO₂ molecules. The adsorption proceeds at oxygen vacancies, during which CO₂ gains electrons from Ti³⁺ forming negatively charged species [4]. The process is accompanied by the transformation of linear structure of CO₂ to a bent form which is highly reactive [5]. It is worth mentioning that the formation of CO₂[−] species can occur without the illumination of the surface of photocatalyst but it significantly increases their concentration [4]. The another important step is the formation of electron–holes pairs when the light strikes the photocatalyst. The formed electrons are transferred to the surface of TiO₂ where they get captured by adsorbed CO₂, thus enhancing the formation of negatively charged species. At the same time, the generated holes come into contact with water molecules, yielding hydrogen ions (H⁺) and hydroxyl radical (·OH). The CO₂[−] radicals can further be converted to CO

✉ Oleksandr Shtyka
oleksandr.shtyka@p.lodz.pl

¹ Institute of General and Ecological Chemistry, Lodz University of Technology, Zeromskiego 116, 90–924 Lodz, Poland

² Institute of Advanced Materials and Technologies, National Research University of Electronic Technology, Shokin Square 1, Zelenograd, Moscow, Russia 124498

via the reaction with $\text{H}^\cdot$ radical, self-transformation, or dissociation on the oxygen vacancy sites [5]. The generated CO serves as the intermediate for the formation of CH_4 and/or CH_3OH . This process can proceed via two different routes, i.e. deoxygenation and hydrogenation. The first path results in the formation of $\text{CH}_3^\cdot$ radical (via deoxygenation of CO and subsequent hydrogenation of $\text{CH}_{(0-2)}$ species) which can either combine with $\text{OH}^\cdot$ radical to form CH_3OH or with $\text{H}^\cdot$ radical to form CH_4 . The latter route involves the formation of HCOOH intermediate which is next transformed to CH_3OH and then to CH_4 [5, 6].

Among various photocatalysts, TiO_2 is one of the most well-known and widely used materials due to its high oxidative efficiency, high chemical stability, nontoxicity and low-cost. Despite the progress made during the last three decades, there are still some unsolved problems. Firstly, the photocatalytic activity of TiO_2 is still low, mainly due to the following two reasons:

- slow reaction rate due to rapid recombination the photogenerated electron–hole pairs;
- poor solar energy utilization due to large band gap energy of 3.2 which limits the absorption of solar radiation to the UV light range accounting for only about 5% of the solar spectrum;

Therefore, a great deal of effort has been devoted to enhancing the photocatalytic efficiency of TiO_2 , such as metal and non-metal doping, depositing of noble metals, dye sensitization, and fabrication of composites with other materials [7].

For example, it is well known that the presence of Ag species on the surface of TiO_2 enhances its photocatalytic activity due to the ability of metal nanoparticles to trap the excited electrons from titanium dioxide, improving the charge carrier separation. Also, the Ag-modified TiO_2 photocatalysts are characterized by better solar energy utilization than TiO_2 itself due to surface plasmon resonance effect in the visible light spectrum [8].

Secondly, most of the photocatalytic experiments on the reduction of carbon dioxide reported in the literature so far have been performed in a stationary liquid phase, and they are characterized by a long time of UV irradiation (up to 24 h) [7, 8]. Also, when the photocatalytic reaction is performed in the batch reactors, the formed products can be re-adsorbed over the surface of the photocatalysts or they can participate in side reactions. This makes it difficult to understand and control the reaction mechanism and also product composition as well [8]. The promising approach was shown by Tahir et al. who design a TiO_2 -coated monolith photoreactor for gas-phase reduction of CO_2 . Their study revealed significant enhancement in the formation of CO which was attributed to higher illuminated surface area,

higher photon energy consumption, and better utilization of reactor volume [9]. Moreover, they managed to significantly enhance the yield of CO (from 43 to 962 mol g-catal.^{−1}) by doping of TiO_2 with indium [9]. Therefore, the development of appropriate reactor design and synthesis method of photocatalysts are of prime importance in the way of scaling up of photocatalytic processes.

The main aim of the work was to study the photocatalytic activity of modified TiO_2 samples under continuous flow conditions. The surface of TiO_2 was modified by deposition of platinum, palladium, nickel, and copper nanoparticles. The effects of type and content of metal on the physicochemical and photocatalytic properties of TiO_2 were investigated.

2 Experimental Part

2.1 Catalyst Preparation

The TiO_2 powder (Degussa, P-25) was purchased from a commercial supplier. The TiO_2 supported catalysts were prepared by traditional wetness impregnation method using aqueous solutions of nitrate salts (for Ni and Cu catalysts), chloroplatinic acid, and palladium(II) chloride. The estimated quantities of the precursor solutions were added dropwise to TiO_2 powder and, then, the obtained mixture was left at ambient overnight. Next, the excess of the solvent was evaporated under a vacuum. Finally, the impregnated samples were dried at 110 °C for 4 h and, afterward, they were calcined at 300 °C for 4 h in an air atmosphere. The nominal metal loading was as follows: 0.5–5% wt. Cu and Ni, 0.5–1% wt. Pt and Pd. Prior the physicochemical measurements (except reducibility) and photocatalytic activity tests, the obtained samples were reduced in hydrogen stream (5% H_2 –95% Ar) for 4 h at 120 °C for copper catalyst, at 300 °C for nickel catalyst, and at 200 °C for palladium and platinum samples.

2.2 Physicochemical Characterization

Surface area, pore volume, and pore size distribution were determined from the nitrogen adsorption/desorption isotherms at −196 °C, using a Sorptomatic 1900 (Carlo Erba Instruments). The samples were previously outgassed at 300 °C and equilibrated under vacuum for at least 4 h before measuring the adsorption–desorption isotherm. Specific surface areas were evaluated from the measured monolayer capacity (Brunauer–Emmett–Teller method) using the range of relative pressure from ~0.05 to 0.33 and the value for nitrogen cross-section 0.162 nm².

The phase composition of pristine TiO_2 and TiO_2 -supported catalyst was investigated by X-ray diffraction analysis. The diffraction patterns were collected using a

PANalyticalX'Pert Pro MPD diffractometer in Bragg Brentano reflection geometry. The diffractometer was equipped with Cu K α radiation source ($\lambda = 1.5418 \text{ \AA}$). Data was collected in the 2θ range of 5° – 90° with a step size of 0.0167° and exposure per step of 27 s. Because the raw diffraction data contain some noise, the background during the analysis was subtracted using the Sonneveld, E. J. and Visser algorithm. The data were then smoothed using a cubic polynomial function.

The secondary ions mass spectra were recorded with a TOF-SIMS IV mass spectrometer manufactured by IONTOF GmbH, Muenster, Germany. The instrument is equipped with Bi liquid metal ion gun and high mass resolution time of flight mass analyzer. Secondary ion mass spectra were recorded from approximately $100 \mu\text{m} \times 100 \mu\text{m}$ area of the spot surface. During measurement analyzed area was irradiated with the pulses of 25 keV Bi $^{3+}$ ions at 10 kHz repetition rate and an average ion current 0.3 pA. The analysis time was 30 s for both positive and negative secondary ions giving an ion dose below a static limit of 1×10^{13} ions/cm 2 . Secondary ions emitted from the bombarded surface were mass separated and counted in time of flight (TOF) analyzer. During the analysis, a low-energy electron flood gun was used to neutralize the charge on the sample surface. The samples were pressed into pellets before measurements.

The reducibility of samples was studied in an automatic TPR system AMI-1 in the temperature range of 25 – 800°C with a linear heating rate of $10^\circ\text{C min}^{-1}$. Samples (weight about 0.05 g) were reduced in hydrogen stream (5% H $_2$ –95% Ar) with a volumetric flow rate of $40 \text{ cm}^3 \text{ min}^{-1}$. Hydrogen consumption was measured as a function of time using a thermal conductivity detector (TCD).

Surface concentrations of acidic and basic sites were determined by temperature-programmed desorption of ammonia (NH $_3$ -TPD) and carbon dioxide (CO $_2$ -TPD). Before TPD experiments, the samples were plugged with helium at 600°C for 60 min in order to remove any contaminations. After cleaning, the samples were cooled and saturated for 20 min. in flow of pure NH $_3$ at 50°C or alternatively CO $_2$ at 50°C . In both cases, the total flow rate was 25 ml/min. Then, the samples were purged in helium flow until a constant baseline level was attained. TPD measurements were performed in the temperature range 100 – 600°C at a rate of 10°C/min using helium as carrier flow. The evolved ammonia or carbon dioxide were detected by an on-line TCD calibrated by the peak area of known pulses of NH $_3$ or CO $_2$.

Infrared spectra were recorded with an IR Tracer-100 FTIR (Shimadzu) spectrometer equipped with liquid nitrogen cooled MCT detector. A resolution of 4 cm^{-1} was used in collecting all spectra. 128 scans were taken in order to achieve a satisfactory signal to noise ratio.

2.3 Photocatalytic Activity Measurement

Photocatalytic measurements were carried out in a continuous flow reactor equipped with a cooling jacket and a quartz window (Fig. 1). The amount of catalyst used for the photocatalytic reaction was 0.2 g for each run. The reactor was also equipped with two paired mercury lamps POLAMP LRF 400W. The temperature of the reactor was maintained at 35°C and the total flow of reaction mixture (5% vol. H $_2$ O/95% vol CO $_2$) was equal to 0.8 ml/min. The first steady-state activity measurements with and without ultraviolet irradiation were taken after at least 2 h on stream.

The analysis of reaction products was performed by means of an on-line gas chromatograph equipped with a flame ionization detector and a VF-5 ms column. The yield of organic compounds was calculated according to the following equations:

$$Y_{\text{compound}} (\mu\text{mol/g h}) = \frac{\text{Molar flow rate}_{\text{compound}}}{g_{\text{catalyst}} \times 60} \quad (1)$$

3 Results and Discussion

3.1 Physicochemical Properties of Supports and Catalyst

The reducibility of modified TiO $_2$ photocatalysts was investigated with the aim to determine the optimum temperatures at which the metal oxides nanoparticles are being reduced. This is necessary to avoid excessive heating during the reduction process which can lead to the agglomeration of deposited metal particles. According to literature, the reduction of pristine TiO $_2$ occurs at a temperature of 400 – 720°C . However, in our case, no detectable hydrogen consumption peaks were detected in this temperature range (Fig. 2).

The TPR profiles of Cu/TiO $_2$ catalysts showed two overlap peaks (P1 and P2) located in the temperature range from 200 to 250°C which can originate either from stepwise reduction of CuO to metallic Cu via formation of Cu $_2$ O intermediate or reduction of highly dispersed copper

Fig. 1 Schematic representation of the reactor

Fig. 2 The TPR- H_2 profiles of modified TiO_2 catalysts

oxidizes (P1) and bulk-like CuO phases (P2) [10, 11]. The reduction of nickel oxide species occurs at a higher temperature of around 250–350 °C. Similarly, as in the case of copper samples, two peaks (P3 and P4) can be distinguished with the maxima at 270 and 300 °C, respectively. The observed hydrogen consumption peaks can be due to either different interaction of nickel oxide species with TiO_2 support or kinetic limitation of the process itself. In the case of copper and nickel catalysts, no hydrogen consumption peaks were observed in the investigated temperature range. The negative peak observed at about 80 °C in the TPR profile of Pd/TiO_2 is attributable to the decomposition of palladium-hydride formed at room temperature at the beginning of the analysis [12, 13]. It is worth mentioning that the absence of hydrogen consumption peak, in this case, does not exclude the presence of the oxidized palladium species as their reduction can occur below room temperature in reducing atmosphere [14].

Based on the results obtained from TPR- H_2 measurement, it was proposed to perform the mild reduction of copper and nickel catalysts at 120 and 300 °C, respectively. At such conditions, some amount of metal nanoparticles remain in the form of oxide which is also photocatalytically active [15, 16]. Also, it was reported that the coexisting of both Cu^+ and Cu^0 facilitates the separation of electron–hole pairs and promotes electron transfer to adsorbed CO_2 [5]. The palladium and platinum samples were reduced at 200 °C to eliminate the chloride species, originating from metal precursors. The oxidation state of investigated samples before and after reduction was evaluated using the TOF-SIMS technique. It is assumed that differences in the oxidation state of metal nanoparticles affect the emission intensity of MeO^- ions containing metal atom Me bonded to oxygen. Negative ions were chosen for analysis as they mainly form

Table 1 Emission intensities of MO^- secondary ions

Samples	Secondary ion	Preparation condition	Number of counts
Ni/TiO_2	NiO^-	As-received	2922
		Reduced	2654
Cu/TiO_2	CuO^-	As-received	34151
		Reduced	8203
Pd/TiO_2	PdO^-	As-received	819
		Reduced	350
Pt/TiO_2	PtO^-	As-received	2127
		Reduced	0

by fragmentation of the structures present on the surface of the catalyst whereas positive ions can be formed by recombination of the atoms emitted from distant sites on the catalyst surface [17]. Table 1 presents intensities of MeO^- secondary ions recorded for the as-received and reduced catalysts. From the obtained result, it can be seen that the emission intensity of MeO^- ions decreased for Cu, Pt and Pd catalyst after reduction in the hydrogen atmosphere thereby indicating that these catalysts were almost completely reduced at given conditions. Since no differences between NiO^- ion emission intensity were observed for as-received and reduced Ni/TiO_2 catalysts, it can be concluded that the nickel nanoparticles did not undergo reduction.

The XRD measurements did not confirm the presence of copper and nickel oxides probably due to their low concentration (Fig. 3). The XRD patterns of the investigated samples showed the presence of characteristic bands of rutile and anatase phases of TiO_2 . The estimated ratio of anatase to rutile was approximately 5:1. Generally, among the various crystalline phase of titania, anatase exhibits a better photocatalytic activity. However, it is worth mentioning that anatase TiO_2 , with a small addition of either rutile or brookite phases, demonstrates enhanced photocatalytic activity compared to pure anatase due to the improved electron and hole separation [11, 18].

The results of BET measurement showed that the pristine TiO_2 had a specific surface area (SSA) of about 57 m^2/g which is similar to that reported in the literature [19]. The SSA of modified TiO_2 catalysts was found to vary insignificantly depending on the type of metal and its amount (Table 2).

The catalytic properties of catalyst are also influenced by the presence of acidic and basic surface sites. Within the Lewis theory framework, Ti^{4+} ions are potential electron charge acceptors, i.e. acids, while O^{2-} anions play the role of conjugated bases. Acid–base interactions between TiO_2 surface and incoming gaseous mixture may lead to activated complexes and promote further reactions. At the same time, stable surface species can be formed that can block the catalytic process. Therefore, the investigation of

Fig. 3 XRD profiles of investigated samples **Table 2** Specific surface area of investigated samples

Sample	Specific surface area (m ² /g)
TiO ₂	57
TiO ₂ calcined at 300 °C	62
0.5% Cu/TiO ₂	60
1% Cu/TiO ₂	58
0.5% Ni/TiO ₂	63
1% Ni/TiO ₂	59
0.5% Pd/TiO ₂	58
1% Pd/TiO ₂	60
0.5% Pt/TiO ₂	51
1% Pt/TiO ₂	46

acid-base properties of TiO₂ and modified TiO₂ samples is of vital importance to understand their catalytic activity.

The strength of acidic and basic sites can be determined by deconvolution of TPD peaks, considering both peak area magnitude and central temperature of each peak. The following types of strength of surface sites were proposed: weak (desorption in the temperature range from 100 to 300 °C), medium (300–450 °C), and strong (450–600 °C). According to the results of TPD-NH₃/CO₂ measurements, the TiO₂ catalysts are acidic in nature (Table 3). The pristine TiO₂ was characterized by the highest amount of acidic sites (527.2 NH₃ μmol/g_{cat}) most of which were of high strength. The concentration of these surface sites was found to decrease after the deposition of metal particles. This may be attributed to the partial coverage of TiO₂ surface by these particles. In

Table 3 Distribution of acid centers for TiO₂ and modified TiO₂ samples

Sample	Weak centers (μmol/g _{cat}) 100–300 °C	Medium centers (μmol/g _{cat}) 300–450 °C	Strong centers (μmol/g _{cat}) 450–600 °C	Total amount of desorbed NH ₃ (μmol/g _{cat}) 100–600 °C
TiO ₂	97.7	191.3	238.2	527.2
0.5% Cu/TiO ₂	24.9	13.3	0.3	38.5
1% Cu/TiO ₂	54.3	45.8	2.0	102.1
0.5% Ni/TiO ₂	84.1	67.2	7.1	158.4
1% Ni/TiO ₂	92.3	110.2	16.0	218.5
0.5% Pt/TiO ₂	54.7	29.4	2.6	86.7
1% Pt/TiO ₂	76.5	72.5	14.0	163.0
0.5% Pd/TiO ₂	80.5	72.6	12.2	165.3
1% Pd/TiO ₂	56.2	86.3	30.5	173.0

the case of the catalysts with high metal loading (of about 1%), the deposited particles are likely to be agglomerated which leads to larger support surface exposed to NH_3 molecules and, thus, to a higher amount of acidic sites.

The similar results were obtained for basic sites. Upon deposition of metal on the surface of TiO_2 , the concentration of basic centers decreased, and the biggest decrease was observed for the catalysts with metal loading of 1%. As discussed earlier, such result might be due to partial masking of TiO_2 surface. It's also worth mentioning that the decrease of existing basic sites in TiO_2 was likely to be offset by the generation of new oxygen vacancies during the reduction of investigated catalysts [20]. As shown in Table 4, the reduction of pristine TiO_2 in the hydrogen atmosphere led to an increase in the total basicity of its surface from 59.6 to 94.8 $\text{CO}_2 \mu\text{mol/g}_{\text{cat}}$.

The key steps of the photocatalytic reduction of carbon dioxide are the adsorption and subsequent activation of reaction reagents. According to Benkoula et al. the water vapor can be adsorbed via four different mechanisms among which the dissociative adsorption at O^{2-} vacancies is recognized as a dominant path [21]. Similarly, the adsorption of CO_2 first proceeds at oxygen vacancies and then, after filling all the oxygen vacancies, at Ti^{4+} sites [22]. Therefore, the reduction in the number of basic sites due to deposition of metal can be considered as a negative effect due to decrease of number of centers available for reactants adsorption.

Table 4 Distribution of basic sites for TiO_2 and modified TiO_2 samples

Sample	Weak centers 100–300 °C ($\mu\text{mol/g}_{\text{cat}}$)	Medium centers 300–450 °C ($\mu\text{mol/g}_{\text{cat}}$)	Strong centers 450–600 °C ($\mu\text{mol/g}_{\text{cat}}$)	Total amount of desorbed CO_2 ($\mu\text{mol/g}_{\text{cat}}$)
TiO_2	42.9	14.6	2.1	59.6
TiO_2 reduced	52.5	38.8	3.5	94.8
0.5% Cu/ TiO_2	15.2	10.5	0.4	26.1
1% Cu/ TiO_2	20.4	15.4	0.8	36.6
0.5% Ni/ TiO_2	41.9	8.1	0.0	50.0
1% Ni/ TiO_2	37.0	13.4	0.3	50.7
0.5% Pt/ TiO_2	24.0	29.5	2.5	56.0
1% Pt/ TiO_2	23.3	24.0	6.4	53.7
0.5% Pd/ TiO_2	23.9	17.2	2.7	43.8
1% Pd/ TiO_2	22.5	9.9	1.5	33.9

3.2 Photocatalytic Activity Measurements

The analysis of the post-photocatalytic reaction mixtures revealed the presence of methanol and small amounts of methane. The other organic compounds and CO could also be formed during the process but were not detected due to apparatus limitations. Therefore, the methanol was chosen as a marker compound to evaluate the photocatalytic activity of TiO_2 and metal modified TiO_2 samples.

The photocatalytic activity of semiconductor depends on numerous factors, including its energy band gap, recombination of formed electron–hole pairs, adsorption properties, crystallinity, and so forth. The results of photocatalytic measurements showed the TiO_2 itself was almost inactive in the process, the methanol formation rate was about 0.027 $\mu\text{mol/g h}$. In comparison to pristine TiO_2 , the metal modified samples displayed higher photocatalytic reaction rate for methanol formation (Fig. 4). Among the catalyst with metal loading of 0.5%, the most active samples were platinum (0.59 $\mu\text{mol/g h}$) and copper (0.17 $\mu\text{mol/g h}$) samples. Such results are in contradiction with those reported previously. Particularly, Nasir Shehzad et al. reported that Cu/ TiO_2 photocatalyst is more efficient in liquid-phase reduction of carbon dioxide while Ni/ TiO_2 in the gas-phase process [23].

In order to verify the obtained results, the additional series of copper and nickel catalysts were prepared with higher metal concentrations. In general, for all investigated samples, the photocatalytic activity gradually decreased with an increase in the content of metal phase (Fig. 5). The exceptions were only 1.5% and 2% Ni/ TiO_2 that demonstrated a relatively high rate of methanol formation above 0.24 $\mu\text{mol/g h}$. It is well known that the metal deposited on the surface of semiconductor can serve as an efficient electron trap preventing electron–hole recombination and thereby favoring the photocatalytic activity. However, above

Fig. 4 The photocatalytic activity of modified TiO_2 samples after 2 h in the reaction stream

Fig. 5 The photocatalytic activity of Ni (black squares) and Cu (gray circles)/TiO₂ samples as a function of metal content after 2 h in the reaction stream

an optimum concentration of metal, the completely opposite effect is observed that significantly limits the photocatalytic activity of samples.

As discussed earlier, the water vapor can compete with CO₂ for surface site adsorption, thus hampering the photocatalytic reduction process. Therefore, it was attempted to perform long-term stability tests of investigated samples for 3.5 h under the same operating conditions as those previously reported. The obtained results revealed the gradual decrease in photocatalytic activity of samples with increasing reaction time (Fig. 6).

For instance, the photocatalytic rate of methanol formation over 2% Ni/TiO₂ decreased from 0.27 (2 h on reaction stream) to 0.17 μmol/g h (3.5 h). The regeneration of

Fig. 6 The photocatalytic activity of modified TiO₂ samples as a function of time in the reaction stream

catalysts, performed at 300 °C for 2 h in the reaction mixture, showed that they exhibit comparable activities as those observed at the beginning of the photocatalytic process. Such results indicate that the reaction products are likely responsible for the reversible deactivation of photocatalysts. In order to confirm this assumption, the in situ IR measurements of 2% Ni/TiO₂ were performed during adsorption of methanol (0.1% methanol in Ar mixture) followed by subsequent purging with Ar either under UV light or upon heating up to 300 °C (Fig. 7).

The adsorption of methanol on the surface of investigated sample resulted in an appearance of characteristic bands at 2951, 2926, 2897, 2847, and 2824 cm⁻¹. According to the literature, the bands at 2926, 2897, 2824 cm⁻¹ can be assigned to the methoxy groups while at 2847 and 2951 cm⁻¹—to formate species [24, 25]. The irradiation of the sample with UV light led only to a slight attenuation in this frequency range. Also, significant intensification of bands at 2359 and 2341 cm⁻¹ were observed which originate from asymmetric stretching vibration of gaseous CO₂. Such result implies that only small amount of methanol was photodegraded to carbon dioxide. The more prominent decrease in absorption intensity of high-frequency bands was observed only upon heating the sample indicating the decomposition and/or desorption of methanol. Therefore, it can be assumed that the formed methoxy species during the photocatalytic process remain mostly on the surface of the catalysts which lead to their reversible deactivation.

4 Conclusions

The modification of TiO₂ by deposition metal particles led to a decreased number of acidic-base sites and an increased rate of methanol formation. Among investigated samples, the Pt and Ni (2%) were found to be the most active. In general,

Fig. 7 IR spectra of 2% Ni/TiO₂ photocatalyst

the photocatalytic activity decreased with increasing metal content and reaction time. The IR studies revealed that UV irradiation had little impact on desorption and decomposition of formed methoxy species on the surface of TiO_2 , therefore, their accumulation is likely to be responsible for the deactivation of photocatalysts.

Acknowledgements This work was supported by the Russian Science Foundation (Project No. 19-19-00595)

Compliance with ethical standards

Conflict of interest The authors have no conflict of interest to declare.

Informed consent The corresponding author has the informed consent of all co-authors in submitting this paper.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

References

- Nahar S, Zain MFM, Kadhum AAH et al (2017) Advances in photocatalytic CO_2 reduction with water: a review. *Materials*. <https://doi.org/10.3390/ma10060629>
- Hong J, Zhang W, Ren J, Xu R (2013) Photocatalytic reduction of CO_2 : a brief review on product analysis and systematic methods. *Anal Methods* 5:1086–1097
- Tjandra AD, Huang J (2018) Photocatalytic carbon dioxide reduction by photocatalyst innovation. *Chin Chem Lett* 29:734–746. <https://doi.org/10.1016/j.ccllet.2018.03.017>
- Raskó J, Solymosi F (1994) Infrared spectroscopic study of the photoinduced activation of CO_2 on TiO_2 and Rh/TiO_2 catalysts. *J Phys Chem*. <https://doi.org/10.1021/j100080a009>
- Liu L, Li Y (2014) Understanding the reaction mechanism of photocatalytic reduction of CO_2 with H_2O on TiO_2 -based photocatalysts: a review. *Aerosol Air Qual Res*. <https://doi.org/10.4209/aaqr.2013.06.0186>
- Karamian E, Sharifnia S (2016) On the general mechanism of photocatalytic reduction of CO_2 . *J CO_2 Util*. <https://doi.org/10.1016/j.jcou.2016.07.004>
- Abdullah H, Khan MMR, Ong HR, Yaakob Z (2017) Modified TiO_2 photocatalyst for CO_2 photocatalytic reduction: an overview. *J CO_2 Util* 22:15–32
- Wu F, Hu X, Fan J et al (2013) Photocatalytic activity of Ag/TiO_2 nanotube arrays enhanced by surface plasmon resonance and application in hydrogen evolution by water splitting. *Plasmonics* 8:501–508. <https://doi.org/10.1007/s11468-012-9418-5>
- Tahir M, Amin NS (2013) Photocatalytic CO_2 reduction and kinetic study over In/TiO_2 nanoparticles supported microchannel monolith photoreactor. *Appl Catal A* 467:483–496. <https://doi.org/10.1016/j.apcata.2013.07.056>
- Mierczynski P, Ciesielski R, Kedziora A et al (2016) Monometallic copper catalysts supported on multi-walled carbon nanotubes for the oxy-steam reforming of methanol. *React Kinet Mech Catal*. <https://doi.org/10.1007/s11144-015-0955-8>
- Qi GX, Zheng XM, Fei JH, Hou ZY (2001) Low-temperature methanol synthesis catalyzed over $\text{Cu}/\gamma\text{-Al}_2\text{O}_3\text{-TiO}_2$ for CO_2 hydrogenation. *Catal Lett* 72:191–196. <https://doi.org/10.1023/A:1009049523210>
- Deshmane VG, Owen SL, Abrokwhah RY, Kuila D (2015) Mesoporous nanocrystalline TiO_2 supported metal (Cu, Co, Ni, Pd, Zn, and Sn) catalysts: Effect of metal-support interactions on steam reforming of methanol. *J Mol Catal A*. <https://doi.org/10.1016/j.molcata.2015.07.023>
- Gurrath M, Kuretzky T, Boehm HP et al (2000) Palladium catalysts on activated carbon supports Influence of reduction temperature, origin of the support and pretreatments of the carbon surface. *Carbon*. [https://doi.org/10.1016/S0008-6223\(00\)00026-9](https://doi.org/10.1016/S0008-6223(00)00026-9)
- Ferrer V, Moronta A, Sánchez J et al (2005) Effect of the reduction temperature on the catalytic activity of Pd-supported catalysts. *Catalysis Today* 107:487–492
- Lu D, Zelekew OA, Abay AK et al (2019) Synthesis and photocatalytic activities of a CuO/TiO_2 composite catalyst using aquatic plants with accumulated copper as a template. *RSC Advances* 9:2018–2025. <https://doi.org/10.1039/c8ra09645g>
- Ku Y, Lin CN, Hou WM (2011) Characterization of coupled NiO/TiO_2 photocatalyst for the photocatalytic reduction of Cr(VI) in aqueous solution. *J Mol Catal A* 349:20–27. <https://doi.org/10.1016/j.molcata.2011.08.006>
- Yu ML (1982) The sputtering of molecular ions from surfaces in secondary ion mass spectrometry. *Appl Surf Sci* 12:196–201
- Su R, Bechstein R, Sø L et al (2011) How the anatase-to-rutile ratio influences the photoreactivity of TiO_2 . *J Phys Chem C*. <https://doi.org/10.1021/jp2086768>
- Wang G, Xu L, Zhang J et al (2012) Enhanced photocatalytic activity of TiO_2 powders (P25) via calcination treatment. *Int J Photoenergy*. <https://doi.org/10.1155/2012/265760>
- Pan X, Yang MQ, Fu X et al (2013) Defective TiO_2 with oxygen vacancies: synthesis, properties and photocatalytic applications. *Nanoscale* 5:3601–3614
- Benkoula S, Sublemontier O, Patanen M et al (2015) Water adsorption on TiO_2 surfaces probed by soft X-ray spectroscopies: bulk materials vs. isolated nanoparticles. *Sci Rep*. <https://doi.org/10.1038/srep15088>
- Tan S, Zhao Y, Zhao J et al (2011) CO_2 dissociation activated through electron attachment on reduced rutile surface. *Phys Rev B* 84:155418
- Shehzad N, Tahir M, Johari K et al (2018) A critical review on TiO_2 based photocatalytic CO_2 reduction system: strategies to improve efficiency. *J CO_2 Util* 26:98–122
- Mierczynski P, Ciesielski R, Kedziora A et al (2014) Novel $\text{Pd-Cu/ZnAl}_2\text{O}_4\text{-ZrO}_2$ catalysts for methanol synthesis. *Catal Lett* 144:723–735. <https://doi.org/10.1007/s10562-014-1201-0>
- Gazsi A, Schubert G, Bánsági T, Solymosi F (2013) Photocatalytic decompositions of methanol and ethanol on Au supported by pure or N-doped TiO_2 . *J Photochem Photobiol A*. <https://doi.org/10.1016/j.jphotochem.2013.08.009>

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.