EFFECT OF CALCINATION TEMPERATURE AND CALCINATION TIME ON THE KAOLINITE/TIO$_2$ COMPOSITE FOR PHOTOCATALYTIC REDUCTION OF CO$_2$

VLIV KALCINAČNÍ TEPLOTY A DOBY KALCINACE NA KOMPOZIT KAOLINIT/TIO$_2$ PRO FOTOKATALYTICKOU REDUKCI CO$_2$

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Abstract

The kaolinite/TiO$_2$ composite (60 wt% of TiO$_2$) was prepared by thermal hydrolysis of a raw kaolin suspension in titanyl sulphate and calcined at different temperatures (600, 650 and 700°C) and for different times (1, 2 and 3 h). The obtained samples were characterized by XRPD, N$_2$ physical adsorption and SEM, and tested for photocatalytic reduction of CO$_2$. The different calcination conditions did not influence TiO$_2$ phase composition, only slightly changed the specific surface area, and significantly affected crystallite size of kaolinite/TiO$_2$ composite. A higher temperature and longer duration of calcination lead to higher crystallinity of the powder. The photocatalytic results showed that the crystallite size determined the efficiency of kaolinite/TiO$_2$ photocatalysts.

Abstrakt

Kompozit kaolinit/TiO$_2$ (60 hm% TiO$_2$) byl připraven termální hydrolýzou suspenze surového kaolinu v síranu titanylu a kalcinován při různých teplotách (600, 650 a 700°C) a po různou dobu (1, 2 a 3 h). Získaný vzorek byl charakterizován pomocí XRPD, N$_2$ fyzikální adsorpcí a SEM, a testován na fotokatalytickou redukci CO$_2$. Rozdíl kalcinačních podmínek neovlivnil složení fáze TiO$_2$, pouze se mírně pozměnila specifická povrchová plocha a výrazně byla ovlivněna velikost krystalitu kompozitu kaolinit/TiO$_2$. Vyšší teplota a delší doba kalcinace vedly k vyšší krystalitě prášku. Fotokatalytické výsledky ukázaly, že velikost krystality určuje účinnost fotokatalyzítoru kaolinit/TiO$_2$.

Key words kaolinite, TiO$_2$, photocatalysis, carbon dioxide, reduction

1 INTRODUCTION

The emission of carbon dioxide into the atmosphere is one of the most serious problems with regard to the greenhouse effect. Therefore, investigators make special effort to find effective methods to reduce CO_2 emissions, and moreover to convert CO_2 into more useful compounds (methane, methanol, ethanol, formic acid etc.). The efficient photocatalytic reduction of CO_2 with H_2O is one of the most desirable and challenging goals in research around the topic of the environment [1-8].

Nano-sized TiO_2 has received great attention as a photocatalyst due to a strong resistance to chemical and photocorrosion, high efficiency, lack of toxicity, and low cost. One of the possibilities regarding how to increase its photocatalytic activity is the introduction of TiO_2 nanoparticles into the clay mineral structure [9]. Preparation, characterization and photocatalytic efficiency for CO_2 photocatalytic reduction of kaolinite/TiO_2 composite was the subject of our recent work [10]. Significantly higher yields of CO_2 reduction products were observed in comparison to a commercial TiO_2 catalyst. Based on these promising results, we decided to provide the detailed study of an effect of kaolinite/TiO_2 composite preparation conditions on physicochemical and photocatalytic properties. Calcination temperature is one of the factors determining these properties.

Hamadanian et al. tested photocatalytic activity of the copper and sulfur codoped TiO_2 photocatalyst for degradation of methyl orange (MO) solutions [11]. The hotocatalytic activity of undoped TiO_2 calcinated at 500–700°C and 0.1% Cu, S-codoped TiO_2 calcinated at 500 and 700–850°C was tested under UV irradiation. Because of the sintering phenomenon, the size of nanoparticles increased while the calcination temperature was increased. Therefore, the surface area and photocatalytic activity decreased.

Mahdjoub et al. studied photoinduced degradation of a mono azo dye methylorange by titania nanopowders [12]. The samples were prepared with the sulphate process and were annealed in air at temperatures of up to 750°C, for 30 min. The X-ray diffraction indicates that the thermal annealing resulted in coarsening the average crystallite size from 13 to 72 nm. The highest photoactivity was observed in material treated at 500°C (average crystallite size was 20 nm).

Jia et al. probed photocatalytic activities of Ni, La-codoped $SrTiO_3$ photocatalysts [13]. The characterization results show that the calcination temperature has a strong influence on the physical–chemical properties of as-synthesized photocatalysts. The surface area and porosity, even the initial adsorption rate for malachite green (MG), decreased with increasing calcination temperature.

Kubacka et al. explored the simultaneous W–N doping of the anatase structure and, particularly, the influence of the calcination temperature in the photoactivity of the samples [14]. Gas-phase photodegradation tests were carried out with two organic pollutants (toluene and styrene). The maximum photoactivity was reached by calcination at 450°C and was concomitantly observed with near complete selectivity to partial oxidation products. Higher calcination temperatures yielded solids with significantly inferior photocatalytic performance.

Zheng et al. investigated photocatalytic degradation of methyl blue (MB) on a P-doped TiO_2 catalyst [15]. The rate constant of the P-doped TiO_2 increased gradually with the increasing calcination temperature of up to approximately 700°C, and decreased at higher calcination temperatures. After calcination at 900°C, the activity of P-doped TiO_2 was smaller, but its kinetic constant was still 2.5 times higher than that one during the calcination at 600°C. In contrast, the photocatalytic activity decreased greatly when the calcination temperature of pure TiO_2 was increased from 600 to 700°C.

The influence of calcination temperature of kaolinite/TiO_2 composite on its photocatalytic against carbon dioxide has not been studied yet. The aim of the presented paper is to investigate the influence of the temperature and duration of kaolinite/TiO_2 composite calcination on the yields of CO_2 photocatalytic reduction in both phases (liquid and gas).

2 EXPERIMENTAL PART

2.1 Kaolinite/TiO_2 composite preparation

The composite kaolinite/TiO_2 containing 60 wt.% of TiO_2 was prepared by a thermal hydrolysis of the suspension of raw kaolin (SAK47, LB minerals) in titanyl sulphate ($TiOSO_4$, Precheza a.s.), described in detail in a work published by Mamulová – Kutlaková et al [16]. The prepared composite was assigned KATI16, number *1* signals the sample in state after drying at 100°C, *6* depicts the content of TiO_2 (60 wt.%). For the purpose of the evaluation of the influence of the KATI16 heat treating conditions on its photodegradation ability against CO_2, KATI16 was calcined for 1h at 600°C to give sample KATI66; at 650°C to give sample KATI(65)6; at 700°C to give sample KATI76. With the aim to describe the influence of the duration of the KATI16 calcination at 600°C on its photodegradation ability against CO_2, the composite KATI16 was calcined at 600°C for 2 and 3 hours to give samples being assigned KATI66(2) and KATI66(3), respectively.

2.2 Characterization of kaolinite/TiO2 catalysts

The phase composition of the prepared samples was studied using the X-ray powder diffraction method (XRPD). The XRPD patterns were recorded under CoKα irradiation using a Bruker D8 Advance diffractometer (Bruker AXS, Germany) equipped with a fast position sensitive detector VÅNTEC 1. Measurements were carried out in a reflection mode, and powder samples were pressed in a rotational holder. The phase composition was evaluated using the database PDF 2 Release 2004 (International Centre for Diffraction Data). The crystallite size *Lc* of anatase was calculated using the Scherrer equation, lanthanum hexaboride (LaB6) was utilized as a standard [17].

The morphology of composite particles was observed on SEM Philips XL 30 (PHILIPS). Samples were coated with an Au/Pd film and the SEM images were obtained using a secondary electron detector. Elemental composition of samples was determined using the energy dispersive X-ray analysis (EDAX).

The specific surface area (SSA) of the powder samples was analyzed by nitrogen adsorption in a NOVA 4000e (QUANTACHROME INSTRUMENTS) nitrogen sorption apparatus. The samples were degassed for 3h at 105°C before the measurement. SSA was determined by the multipoint BET method using the adsorption data in the relative pressure range of 0.1 - 0.3.

The content of sulfur was determined using the CS244 carbon/sulfur determinator (LECO Corporation) equipped with the HT1000 induction furnace. The combustion process was carried out in ceramic crucibles filled with 1g of flux LECOCEL (tungsten particulates) and 1g of iron chip accelerator.

2.3 Photocatalytic reduction of CO2

The photocatalytic reduction of carbon dioxide was carried out in a homemade apparatus equipped with a stirred batch annular reactor with a suspended catalyst illuminated by a UV 8W Hg lamp (254 nm). The gas chromatograph (GC) equipped with flame ionization and thermal conductivity detectors (FID, TCD) were used for the analysis of gas and liquid reaction products. The details of the photocatalytic CO_2 reduction experiment and analytical methods were described in our previous publication [18]. It is important to minimize the influence of transport phenomena during kinetic measurements. The elimination of CO_2 diffusion from the bulk of gas through the gas–liquid interface in a laboratory batch slurry reactor was accomplished by saturating the liquid with pure CO_2 before the reaction started [2, 3]. Catalyst loading of 1g . dm^{-3} was chosen to avoid concentration gradients in the bulk of stirred liquid with kaolinite/TiO_2 suspension due to the scattering effect of light caused by the high catalyst concentration [3, 4, 19, 20]. The determination of a suitable volume of the liquid phase in our annular photoreactor to fulfill the requirement of perfect mixing has been published recently as 100 ml [21].

3   RESULTS AND DISCUSSION

3.1 Characterization of kaolinite/TiO_2 nanoparticles

The X-ray diffraction pattern registered for all the samples of kaolinite/TiO_2 reveals the presence of kaolinite, quartz, mica and anatase (Fig. 1). The kaolinite (001) basal diffraction line disappeared in all patterns of the calcined samples. This fact is attributed to the dehydroxylation of the kaolinite structure, which leads to the formation of an amorphous phase called metakaolinite. Another significant feature is the sharpening of anatase diffraction peaks related to the growth of the anatase crystallite size and increase of anatase content.
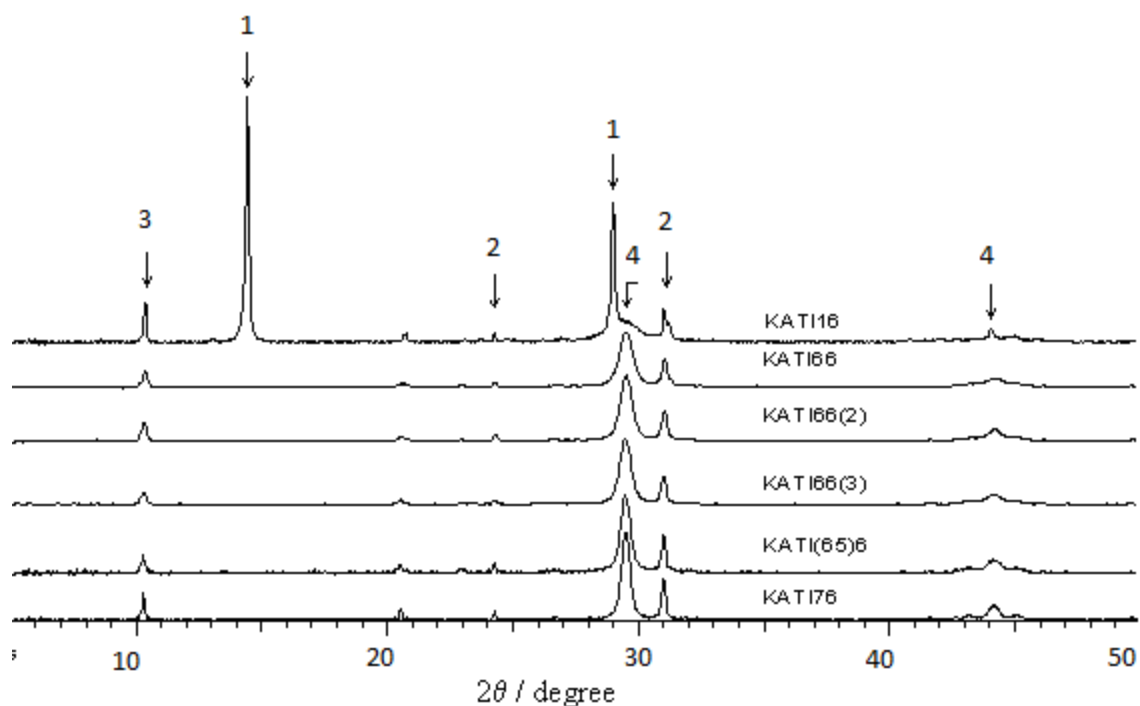
Fig. 1 XRPD of the original composite KATI16 and KATI16 calcined at the different temperatures (600°C, 650°C and 700°C) and for different calcination time (1, 2 and 3 hours). 1 … kaolinite, 2 … quartz, 3… mica, 4 anatase.

The crystallite size is closely related to the calcination temperature (Tab. 1) as well as to the duration of the calcination at a given temperature as shown in Tab. 2, and the same relationship is true for sulphur content.

Tab. 1 Selected characteristics of kaolinite/TiO2 catalysts calcinated at different temperatures

	Calcination temperature (°C)	Crystallite size (nm)	S_{BET} ($m^2 . g^{-1}$)	SO_3 (wt. %)
KATI16	dried	6*	65	3.50
KATI66	600°C	18	39	2.48
KATI(65)6	650°C	27	29	0.73
KATI76	700°C	34	24	0.35

*The calculation of crystallite size was not feasible due to the overlapping of the 101 anatase diffraction line and 002 kaolinite diffraction line. The value was extrapolated from a specific surface area–crystallite size relation.

The increase of the calcination temperature caused the decrease of the specific surface area and the increase of kaolinite/TiO$_2$ crystallite size. The dried catalyst KATI16 had the highest specific surface, and the catalyst calcined at 600ºC (KATI66) had the smallest crystallite size.

Tab 2. Selected characteristics of kaolinite/TiO2 catalysts calcinated at 600ºC with different duration of calcination

	Duration of calcination (hour)	Crystallite size (nm)	S_{BET} ($m^2 . g^{-1}$)	SO_3 (wt. %)
KATI66	1	18	39	2.48
KATI66(2)	2	22	34	1.21
KATI66(3)	3	23	33	1.13

The increasing duration of calcination increased the crystallite size and decreased the sulphur impurity content of kaolinite/TiO_2 catalysts. The specific surface area decreased with the duration of calcination only slightly. The highest changes of the crystallite size, specific surface area and impurity content were registered for the catalyst with a calcination duration of 1 and 2 hours (KATI66 a KATI66(2)) while the changes, when calcination was longer than 2 hours, were minimal (KATI66(2) and KATI66(3)).

The morphology of the kaolinite sample and KATI66 sample that was studied using the scanning electron microscopy is illustrated in Fig. 2. It is evident from this image that TiO_2 particles preferably grow on the kaolinite particles' edges. This observation implies the idea that the rigid, smooth surface of kaolinite particles without cracks are not a suitable matrix for a TiO_2 nanoparticles growth. This observation is in contrast with the observation proposed by Chong et al. who prepared a 7 nm thick compact layer using titanium (IV) tetraisopropoxide as a TiO_2 precursor [22].
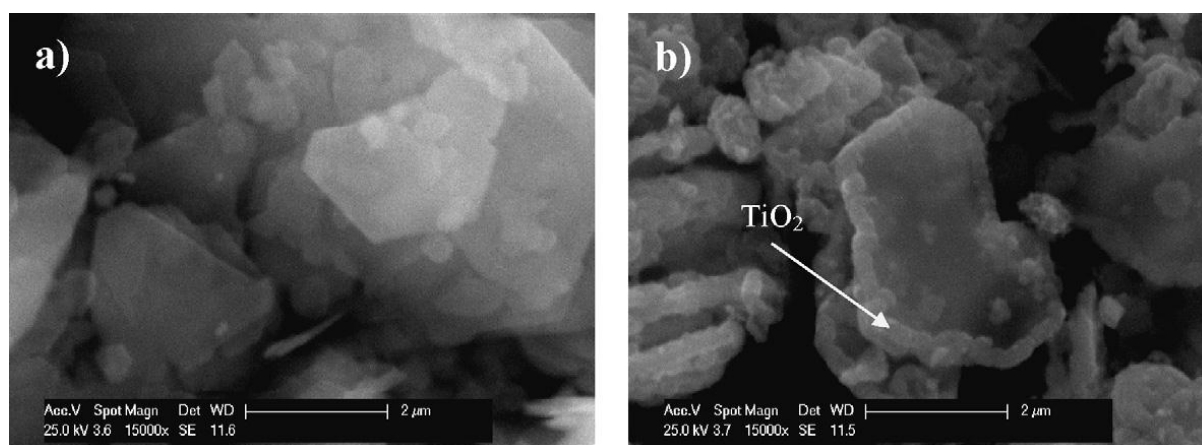

Fig. 2 SEM micrograph of kaolinite (a) and sample KATI66 (b).

3.2 The photocatalytic reduction of CO_2

The effect of irradiation time on the formation of CO_2 photocatalytic reduction products was investigated over a period of 0 – 24h on kaolinite/TiO_2 catalysts calcined at different temperatures and for different calcination time. Fig. 3 shows the evolution of all reaction products as the functions of the irradiation time for the KATI66 catalyst. Two main products were determined: methane in the gas phase and methanol in the liquid phase. Hydrogen and low amounts of carbon oxide were also detected. Other products such as formic acid, formaldehyde, ethane and ethylene could also be formed [1, 4], but they were undetectable. The observed order of yields ($\mu mol . g^{-1} . cat$) was: $H_2 > CH_4 > CH_3OH \geq CO$.
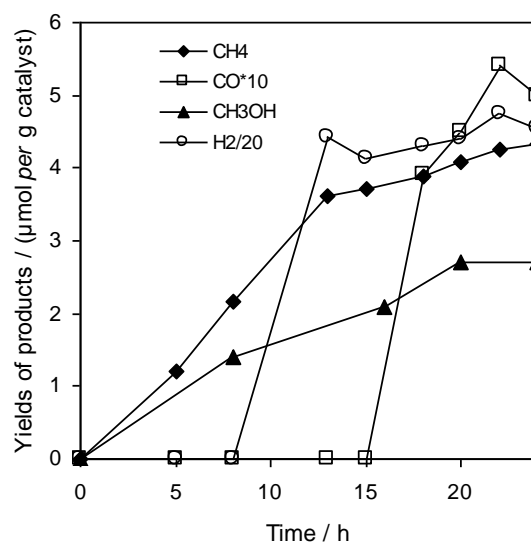
Fig. 3 Time dependence of the product yields of CO_2 photocatalytic reduction over the KATI66 catalyst.

3.3 Effect of calcination temperature

Comparisons of CH_4, CH_3OH and H_2, CO yields over kaolinite/TiO_2 calcined at different temperatures are shown in Fig. 4A, B and 5A, B, respectively. The yields of methane were negligible during the first 8h of irradiation in all cases with the exception of the most active KATI66 catalyst (Fig. 4A). A similar trend of CH_4 yield-time dependency was observed over all catalysts.

A

B
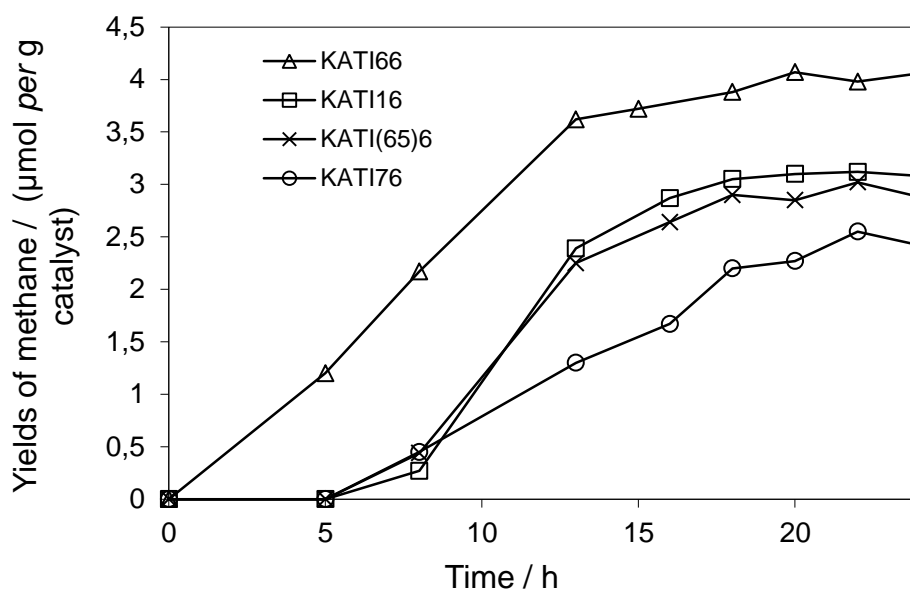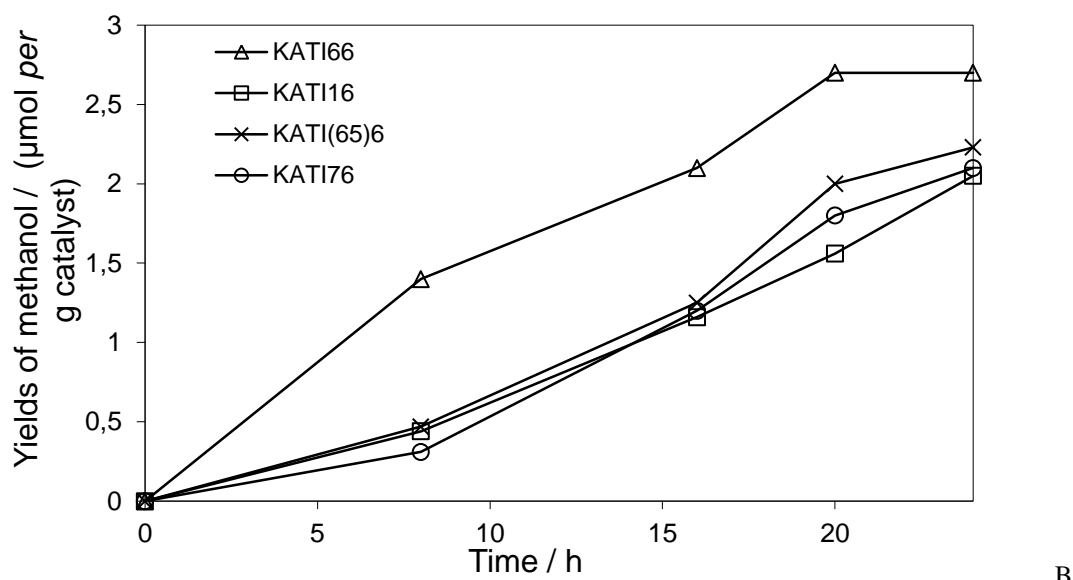
Fig. 4 Time dependence of methane (A) and methanol (B) yields over the kaolinite/ TiO$_2$ catalysts calcined at different temperatures.

The yields of methanol were lower than the yields of methane (Fig. 4B). Incipient methanol can act as a sacrificial agent and in part can be completely oxidized to carbon dioxide and H$_2$ [23, 24]. The data at 5 hours were measured but were under the limit of determinableness which was determined as 12 μg CH$_3$OH *per* L (i.e. 0.38 μmol CH$_3$OH *per* g catalyst). The steepest curve of methanol yield was measured for the KATI66 catalyst.

The hydrogen yields were not detected during the first 5 h of irradiation in all cases (Fig. 5A). After 5 h the hydrogen yields started to increase with the exception of the KATI76 catalyst. The yields of carbon monoxide increased after the first 5 h of the reaction over all catalysts with the exception of the KATI66 catalyst, formation of CO over this catalyst did not start until 16 h of the reaction. However, all CO yields were near the limit of detection (Fig. 5B). The most effective catalyst regarding main products was KATI66, which had a calcination temperature of 600°C.
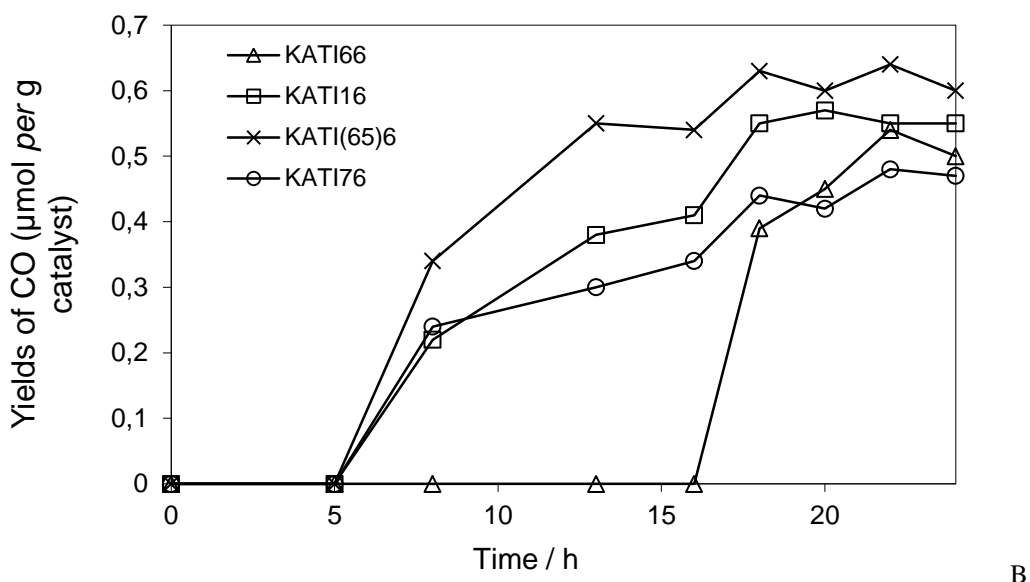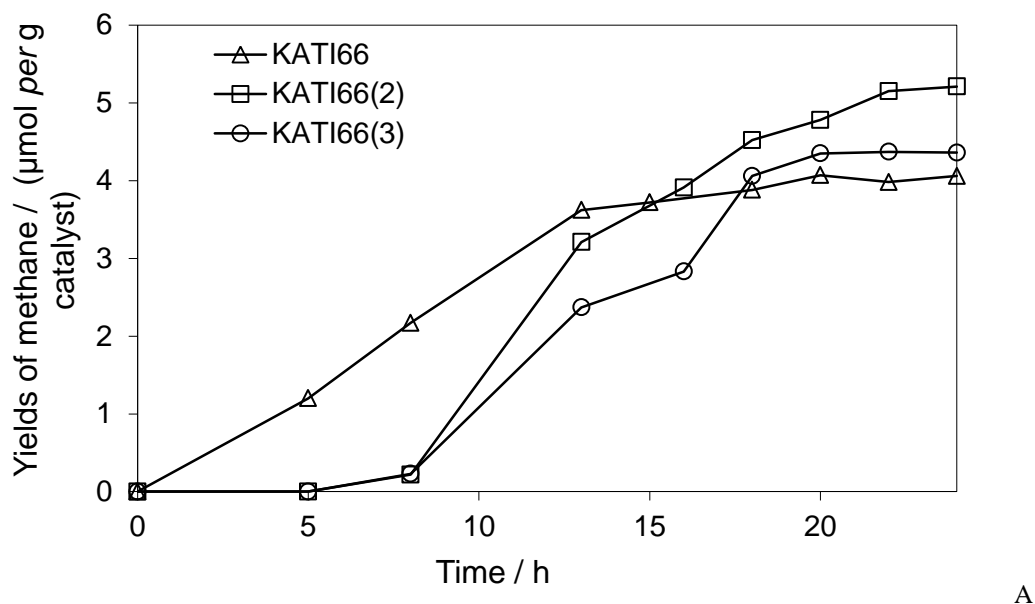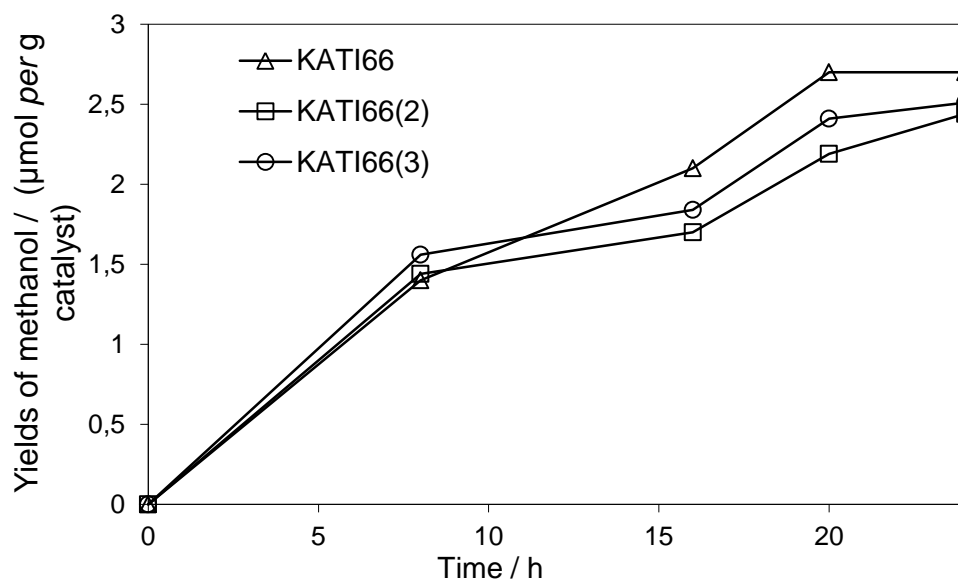

A
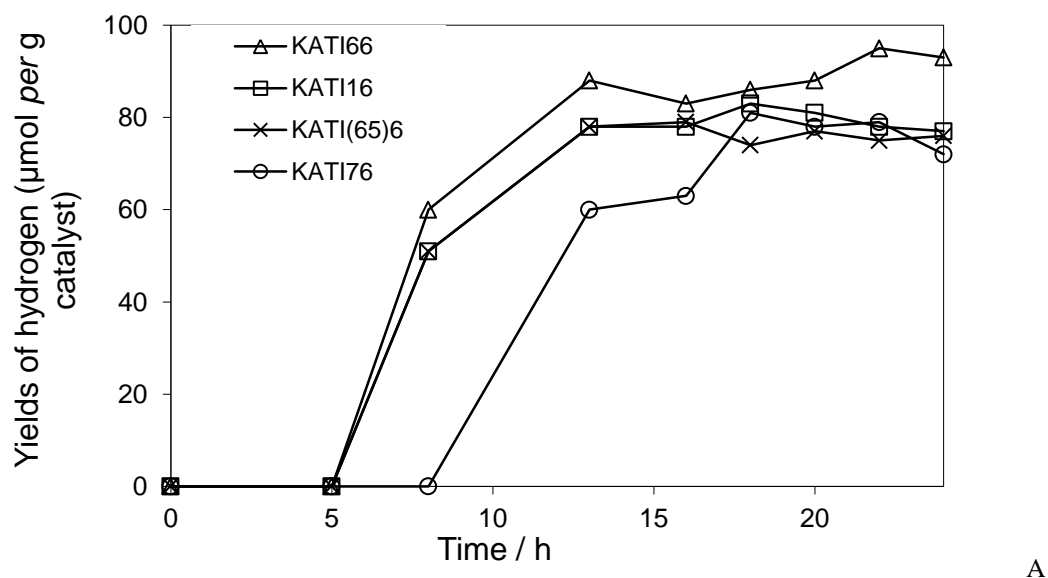
Fig. 5 Time dependence of the hydrogen (A) and the carbon monoxide (B) yields over the kaolinite/ TiO_2 catalysts calcined at the different temperatures.

3.4 Effect of calcination duration

The catalyst with the best photocatalytic activity – KATI66 – was calcined for a different time (1, 2 and 3 h) at 600ºC. Comparisons of CH_4, CH_3OH and H_2, CO yields are shown in Fig. 6A, B and 7A, B, respectively. The yields of methane were negligible during the first 8 h of irradiation for the catalysts KATI66(2) and KATI66(3) (Fig. 6A). The highest yield of methane after 24 h of irradiation was observed over the KATI66(2) catalyst. The yields of methanol were almost the same (Fig. 6B).
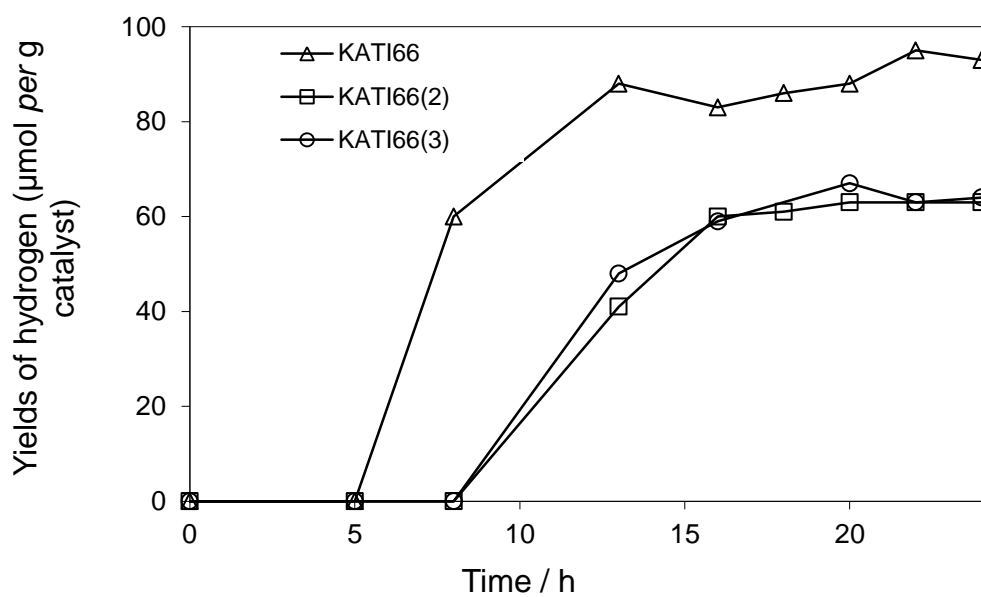
B

Fig. 6 Time dependence of methane (A) and methanol (B) yields over the kaolinite/TiO$_2$ catalysts calcined for different calcination time.

The hydrogen yields and yields of carbon monoxide are showed in Fig. 7A, B. A similar trend of yield-time dependencies of both products was observed for both KATI66(2) and KATI66(3). These yields on KATI66(2) and KATI66(3) are higher than over KATI66 in the case of CO and lower in the case of H$_2$.
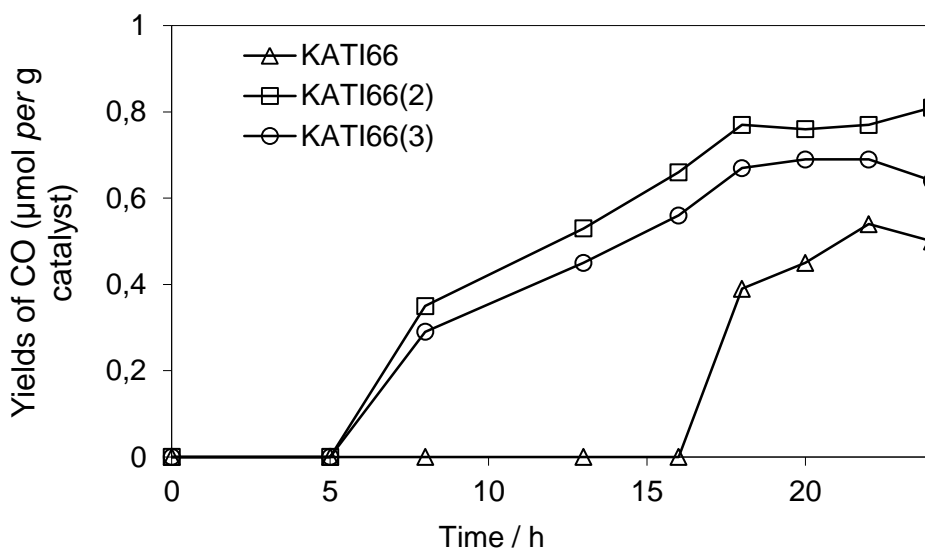

A

Fig. 7 Time dependence of the hydrogen (A) and the carbon monoxide (B) yields over the kaolinite/ TiO_2 catalysts calcined for different calcination time.

Generally, all studied physicochemical characteristics; phase composition, specific surface area, crystallite size and sulphur impurity contents can influence photocatalytic properties of kaolinite/TiO_2 catalysts. In our case, different conditions of calcination did not change the TiO_2 phase composition. Specific surface areas of calcinated composites were lower in comparison to a dried one. However, different calcination conditions (temperature, duration) did not change the specific surface area substantially; their deviations were close to the experimental error ($\pm$ 10%). For the above mentioned reasons, the specific surface area and phase composition of kaolinite/TiO_2 composites calcined at different conditions were not the main parameters that determined their photocatalytic activity.

For examination of the effect of crystallite size on CO_2 photocatalytic reduction efficiency, the yields of CH_4, CH_3OH and CO after 24 hours irradiation for all tested catalysts were compared (Fig. 8). The data from the longest reaction time span were chosen for the photoactivity comparison because the yields of all products were the highest and their GC analysis was the most accurate. It is obvious from the Fig. 8 that the photoreactivity of kaolinite/TiO_2 increases when the crystallite size is increased from 6 nm to 22 nm, but decreases when it is further increased to 34 nm. The yields of all products were the highest over the catalysts with a crystallite size of 18-23 nm; these samples were calcined at 600°C for different times (1h, 2h a 3 h). The crystallite size influenced the dynamic of e^-/h^+ recombination, and so influenced the efficiency of photocatalytic reactions.
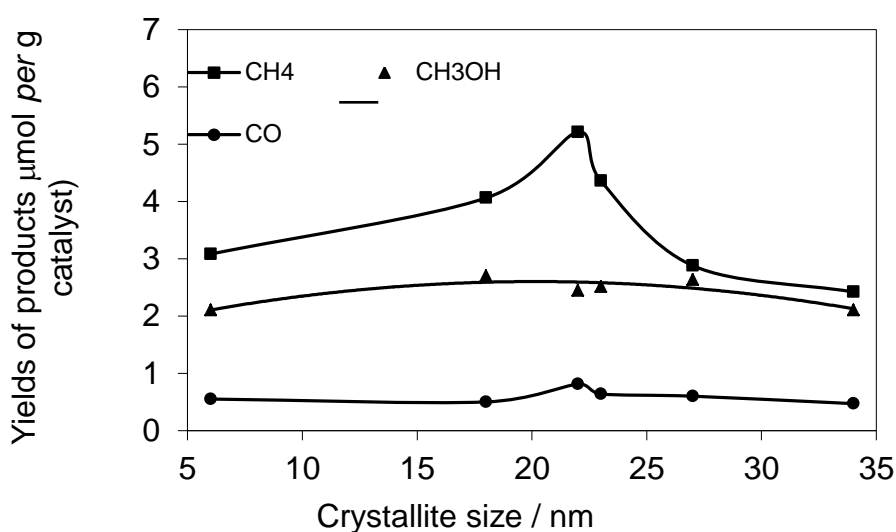

Fig 8. Dependence of the product yields (after 24 hours of irradiation) on different catalysts.

The optimal value of the primary particle size for pure TiO_2 (14 nm) was found in our recent work dealing with the CO_2 photocatalytic reduction [18]. An optimum crystallite size corresponding to the highest

yields was also found for other photocatalytic reactions which depend on the oxidation potential of photogenerated holes, e.g. the degradation of trichloroethylene (with an optimal crystallite size of 7 nm) [25], phenol (with an optimal crystallite size of 25-40 nm) [26], trichlormethane (with an optimal crystallite size of 10 nm) [27], congo red (with an optimal crystallite size of 10 nm) [28]. From the results in Tab. 1 and Tab. 2, it is evident that the sulphur impurity contents decreased with an increase of temperature and duration of calcination. However, this parameter probably was not predominant for photocatalytic activity of kaolinite/TiO_2 composites.

4 CONCLUSIONS

The influence of calcination conditions (the temperature and duration) of the kaolinite/TiO_2 composite on the physicochemical properties and on the yields of CO_2 photocatalytic reduction was studied. It was determined that different calcination conditions did not influence TiO_2 phase composition; only anatase diffraction lines were found in all kaolinite/TiO_2 samples. A slight decrease of specific surface area was observed for the calcinated kaolinite/TiO_2 composite compared to that of a noncalcinated kaolinite/TiO_2 composite. The crystallite size was closely related to the temperature as well as to the duration of the calcination. The crystallite size increased with an increase of the calcination temperature and duration. The photocatalytic results showed that the crystallite size plays an important role in the nanocrystalline kaolinite/TiO_2 composite. The yields of all products were the highest over the catalysts with a crystallite size of 18-23 nm; these samples were calcined at 600°C for different times (1 h, 2 h a 3 h).

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RESUMÉ

Kompozit kaolinit/TiO$_2$ (60 hm% TiO$_2$) byl připraven termální hydrolýzou suspenze surového kaolinu v síranu titanylu a kalcinován při různých teplotách (600, 650 a 700°C) a po různou dobu (1, 2 a 3 h). Získaný vzorek byl charakterizován pomocí XRPD, N$_2$ fyzikální adsorpcí a SEM, a testován na fotokatalytickou redukci CO$_2$. Rozdíl kalcinačních podmínek neovlivnil složení fáze TiO$_2$, pouze se mírně pozměnila specifická povrchová plocha a výrazně byla ovlivněna velikost krystalitu kompozitu kaolinit/TiO$_2$. Vyšší teplota a delší doba kalcinace vedly k vyšší krystalitě prášku. Fotokatalytické výsledky ukázaly, že velikost krystality určuje účinnost fotokatalyzítoru kaolinit/TiO$_2$.