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Comparison of the pure TiO_2 and kaolinite/TiO_2 composite as catalyst for CO_2 photocatalytic reduction

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ABSTRACT

The kaolinite/TiO_2 composite was prepared using thermal hydrolysis of kaolinite/titanyl sulphate suspension and characterized by XRFS, XRPD, SEM and N_2 physical adsorption. Its photocatalytic properties were evaluated by photocatalytic reduction of CO_2 by water and compared with commercial TiO_2 photocatalyst Degussa P25. Results showed that the yields of CO_2 photocatalytic reduction products methane and methanol were higher over a kaolinite/TiO_2 composite than over commercial TiO_2 (Degussa P25) in spite of smaller proportion of TiO_2 in the composite. Introducing of TiO_2 nanoparticles into the kaolinite structure caused a decrease of anatase crystallite size. Kaolinite can also change acidobasic properties of catalyst surface, inhibit the recombination of electron–hole pairs and prevent the formation of TiO_2 aggregates in suspension. These facts can contribute to the observed higher photocatalytic efficiency of kaolinite/TiO_2 compared to the commercial TiO_2 photocatalyst.

1. Introduction

The greenhouse gases such as CO_2, CH_4, N_2O and CFCs are the primary causes of global warming. Recently, the concentration of carbon dioxide in the atmosphere has increased as a result of human activities, further accelerating the greenhouse effect. Efficient photocatalytic reduction of CO_2 by H_2O is one of the most desirable and challenging goals in the research of environmentally friendly technologies [1–16].

Nanosized TiO_2 has received great attention as a photocatalyst due to high efficiency, lack of toxicity and low cost. One of the possibilities to increase its photocatalytic activity is to introduce TiO_2 nanoparticles into the clay mineral structure [17]. By preparing these composites we generally obtain other two advantages: (i) TiO_2 nanoparticles are fixed on the surface of a suitable particulate matrix with particle size in the order of micrometers, which makes manipulation with photocatalytical material easier and (ii) the possible environmental impact caused by the release of nanosized particles is diminished due to higher sedimentation tendency of composites.

Clay minerals belong to often studied functional materials with wide range of applications. Montmorillonite (MMT) belongs to the 2:1 group of phyllosilicates and with respect to its high sorption capacity finds application as a valuable sorbent. MMT also represents the most studied phyllosilicate as a carrier for TiO_2 nanoparticles and the improved photocatalytic activity of TiO_2/MMT composites was shown, e.g. by Kameshima et al. [17]. Kaolinite (KA) belongs to the 1:1 group with great application possibility, e.g. in the ceramic industry, paint industry and cosmetics. Chong et al. [18] used pretreated kaolinite as a support for TiO_2 layers with 7 nm thickness. Obtained kaolinite/TiO_2 composite demonstrated enhanced photocatalytic ability for the removal of Congo red and was mentioned as the highly valuable and easily separable photocatalyst for waste water treatment.

The aim of this work is to compare a photocatalytic reduction process of CO_2 using two catalysts: (i) kaolinite/TiO_2 composite and (ii) commercial TiO_2 (Degussa P25). Montmorillonite is the most studied phyllosilicate as a matrix for the growth of TiO_2 nanoparticles, as is evident from the number of research works on this subject. In spite of this fact we selected kaolinite which finds wider industrial application (paint industry, ceramic industry, industry of building materials, cosmetic, etc.) as a matrix for growing TiO_2 nanoparticles. The photocatalytic reduction of CO_2 in our experimental arrangement runs in liquid phase with suspended catalysts and the reduction products are analyzed in both phases.

2. Experimental

2.1. Kaolinite/TiO_2 preparation

The kaolinite/TiO_2 (KATI66) powder was prepared using thermal hydrolysis of suspension containing kaolinite (KA, LB Minerals)

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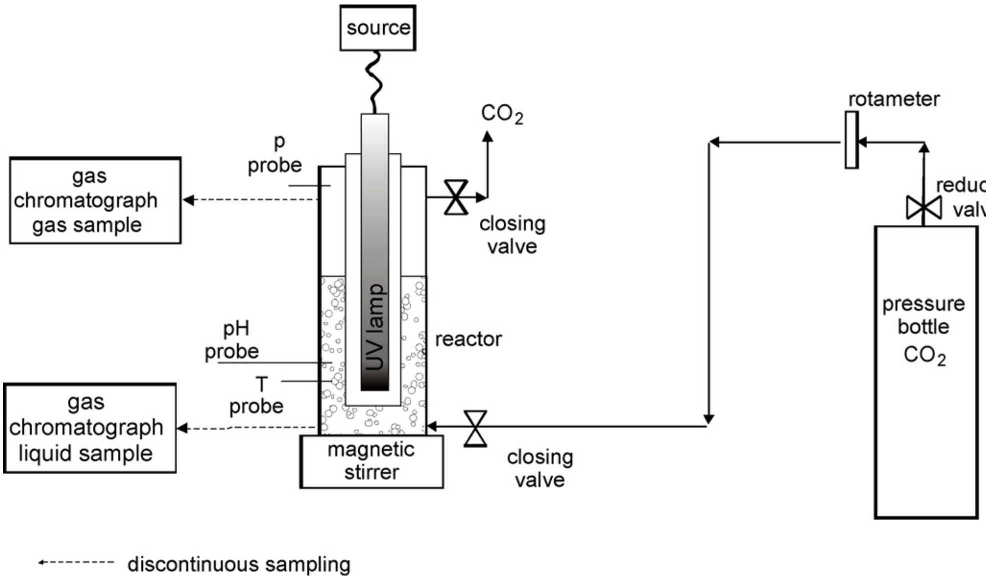

Fig. 1. Block scheme of the apparatus for CO_2 photocatalytic reduction.

and titanyl sulphate ($TiOSO_4$, Precheza a.s.). Kaolinite in as received state was dried at 100 °C for 2 h before its usage; $TiOSO_4$ was delivered in the form of colloid suspension with the following composition: 9.8 wt.% of TiO_2, 50.0 wt.% of H_2SO_4 and 40.2 wt.% of H_2O and was used without any other treatment. The first step of KATI66 preparation comprised of preparating a KA (30 g) + $TiOSO_4$ (460 g) suspension and its 15 min long stirring at laboratory temperature using an electromagnetic stirrer. During the next step the suspension was heated to 95 °C; after reaching this temperature the suspension was hydrolyzed by 130 ml of distilled water which was added dropwise. After 90 min of thermal hydrolysis, the obtained white suspension was cooled to laboratory temperature, the liquid portion was removed by decantation and washed several times using distilled water. Each washing was followed by decantation until the conductivity of the supernatant liquor reached 1 mS/cm^{-2}. The last separation of liquid portion was performed using filtration. The solid portion was dried at 100 °C, then calcined for 1 h at 600 °C and the final composite labelled as KATI66 was obtained.

2.2. Characterization of kaolinite/TiO_2 catalyst

The amount of TiO_2 in the KA and KATI66 samples was determined by X-ray fluorescence spectroscopy (XRFS) using a SPECTRO XEPOS Instrument. For this measurement the sample was pressed to the form of a tablet (wax was used as the binder).

The crystalline phases of the samples were determined by X-ray powder diffraction method (XRPD) using Bruker D8 Advance equipped with a VÅNTEC 1 position-sensitive detector. The crystallite size *Lc* was calculated using the Scherrer equation; lanthanum hexaboride (LaB_6) was set as the standard.

The surface morphology of raw KA and the prepared KATI66 composite was studied using a Philips XL-30 Scanning Electron Microscope. The sample was coated with an Au/Pd film and the SEM images were obtained using a secondary electron detector.

The specific surface area (S_{BET}) of the powder samples was analyzed by nitrogen adsorption in a NOVA 4000e (Quantachrome Instruments, USA) nitrogen sorption apparatus. The sample was degassed for 3 h at 105 °C prior to the nitrogen adsorption measurements. S_{BET} was determined by a multipoint BET method using the adsorption data in the relative pressure range of 0.1–0.3.

2.3. Photocatalytic reactivity experiments

The photocatalytic reduction of carbon dioxide was carried out in a homemade apparatus using a stirred batch annular reactor with a suspended catalyst illuminated by UV 8 W Hg lamps (254 nm) (Fig. 1).

GC/FID/TCD was used for the analysis of gas and liquid reaction products. All data were measured twice and relative error was 5%. The details of the photocatalytic CO_2 reduction experiment and the analytical methods were described in our previous publication [19].

3. Results and discussion

3.1. Characterization of kaolinite/TiO_2 nanoparticles

The measured X-ray diffraction patterns of raw KA, the KATI66 composite and commercial TiO_2 Degussa P25 are shown in Fig. 2. Dehydroxylation of the kaolinite matrix in the KATI66 composite is evident mainly by the disappearing of (0 0 1) and (0 0 2) basal diffraction peaks of kaolinite for which observed maxima for Co K(α1) irradiation are centred at 14.42 and 28.99° 2θ, respectively. The disappearing of these diffraction peaks signalizes the formation of metakaolinite. The presence of typical impurities of raw kaoline, mica and quartz, were also verified on the diffraction pattern of the KATI66 composite together with diffraction peaks belonging to anatase, the presence of rutile was not verified in this composite. On the diffraction pattern of the Degussa P25 sample diffraction peaks belonging to both most common phases of TiO_2 anatase and rutile were observed.

The morphology of the KA and KATI66 samples studied using scanning electron microscopy is depicted in Fig. 3(a) and (b), respectively. From these images it is evident that the originally smooth edges of kaolinite plates in the KA sample (see Fig. 3a) are covered with TiO_2 particles in the case of the KATI66 composite. TiO_2 nanoparticles grow preferably on the kaolinite particle edges (see Fig. 3b). This observation implies that the rigid smooth surface of kaolinite particles without cracks is not a suitable matrix for the growth of TiO_2 nanoparticles. This is in contrast with the results of Chong et al. [18] who prepared a 7 nm thick compact layer using titanium(IV) tetraisopropoxide as a TiO_2 precursor.

The commercial TiO_2 (Degussa P25) is often used as a standard for the comparison of photocatalytic efficiency and its selected

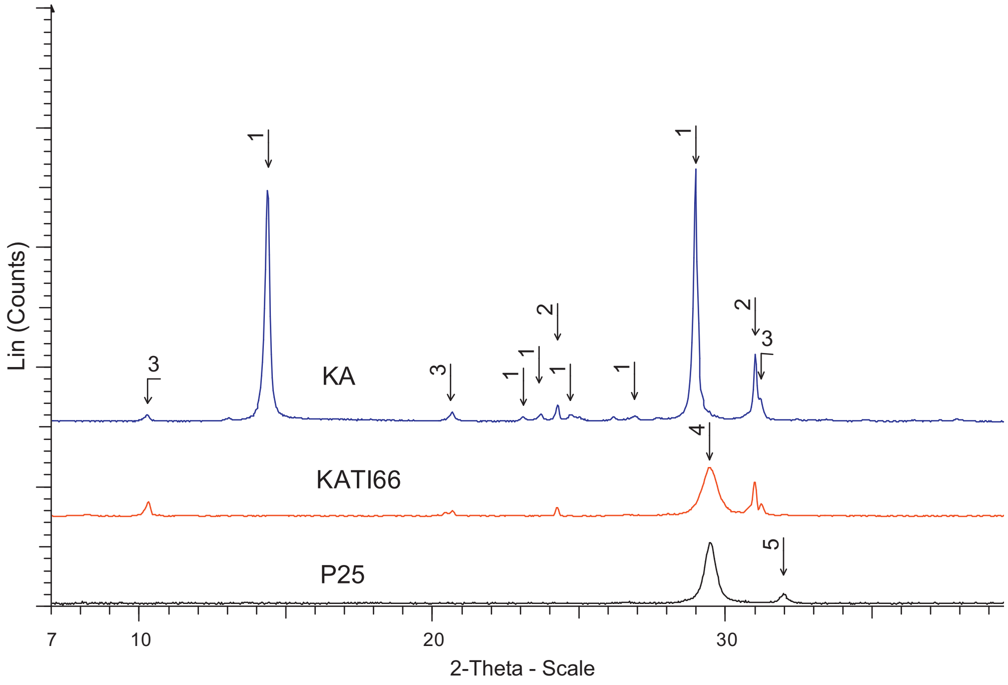

Fig. 2. X-ray powder diffraction patterns of the KA, KATI66 and Degussa P25 samples (1 ... kaolinite, 2 ... quartz, 3 ... mica, 4 ... anatase, 5 ... rutile). The intensities registered for sample KA were multiplied by 0.5.

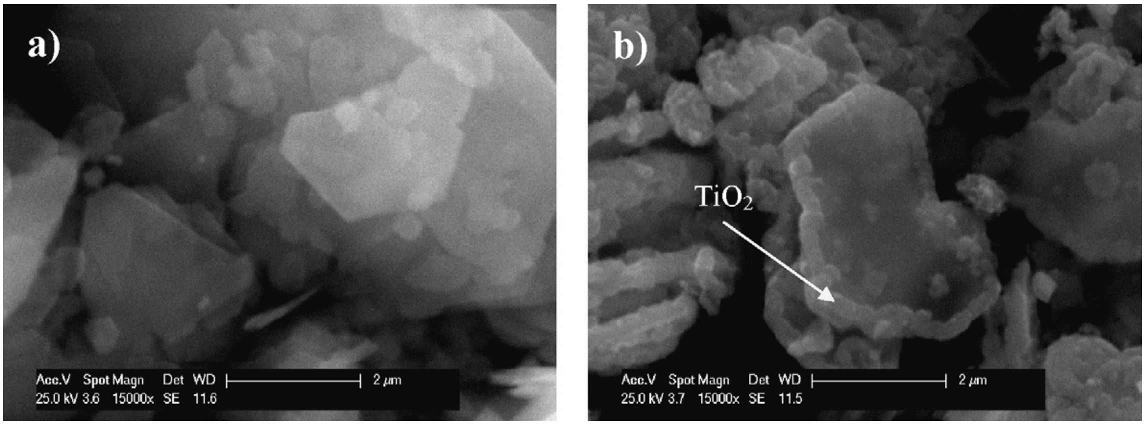

Fig. 3. SEM micrograph of samples: (a) KA and (b) KATI66.

properties are compared with those obtained for raw kaolinite KA and the KATI66 composite in Table 1.

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 0–24 h on both catalysts KATI66 and TiO_2 Degussa P25. Fig. 4 shows the evolution of all reaction products (with the exception of O_2) as functions of the irradiation time for the KATI66 catalyst. Two main products were determined: methane in gas phase and methanol in liquid phase; traces of carbon monoxide were also detected. High amount of hydrogen was formed from the photocatalytic splitting of water. The observed order of yields ($\mu mol/g_{cat}$) was: $H_2 > CH_4 > CH_3OH > CO$.

Table 1
Selected characteristics of catalysts and raw kaolinite.

Sample	Degussa P25	KATI66	KA
S_{BET} ($m^2 g^{-1}$)	50[a]	40	9.5
Lc[b] (anatase) (nm)	26	18	–
TiO_2 content (wt.%)	99.4	60.0[c]	1.15[c]
Anatase (%)	75	100	–
Rutile (%)	25	0	–

[a] Average value given by the manufacturer.
[b] Crystallite size.
[c] TiO_2 content measured using XRFS.

The data from the longest reaction time span were chosen for the comparison of KATI66 with Degussa P25 because these GC analyses of products were the most accurate. The effect of kaolinite presence on the product yields normalized per mass of catalysts is depicted in Fig. 5. Observed yields of all the measured products were higher over the kaolinite/TiO_2 composite than over TiO_2 Degussa P25 despite the fact that the content of photocatalytically active TiO_2 is lower in the composite catalyst.

Fig. 6 compares the yields of the main products of CO_2 photocatalytic reduction normalized per 1 g of TiO_2. It is evident that the activity of the KATI66 catalyst remains higher even if the compared

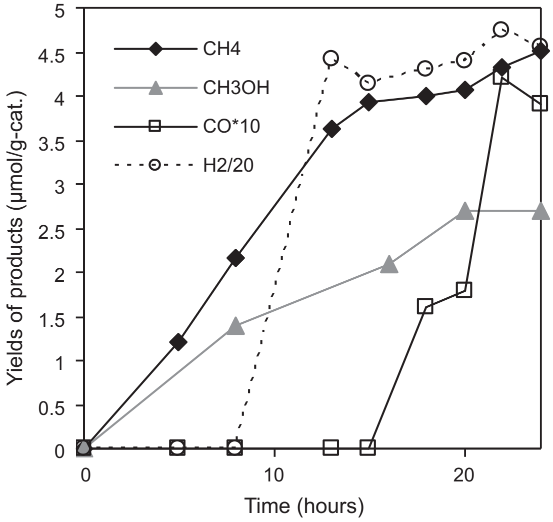

Fig. 4. Time dependence of the CO2 photocatalytic reduction product yields over the KATI66 catalyst. *Conditions*: 8 W Hg lamp, CO_2 pressure at carbonation of 110 kPa, 100 ml of 0.2 M NaOH, catalyst concentration of 1 g l^{-1}, pH 7.

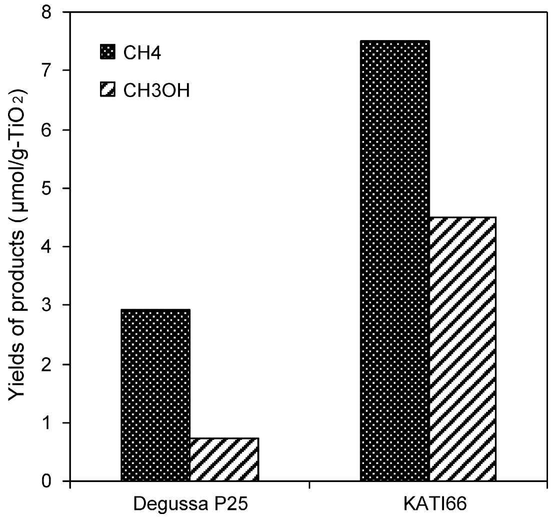

Fig. 6. Dependence of the CO_2 photocatalytic reduction product yields normalized with the TiO_2 mass over KATI66 and Degussa P25 catalysts. *Conditions*: 24 h of irradiation time, 8 W Hg lamp, CO_2 pressure at carbonation of 110 kPa, 100 ml of 0.2 M NaOH, catalyst concentration of 1 g l^{-1}, pH 7.

yields are normalized per the unit content of the catalytically active TiO_2. This indicates that the TiO_2 in the kaolinite/TiO_2 composite catalyst is more effective for the photocatalytic reduction of CO_2 than the TiO_2 in the Degussa P25 commercial catalyst.

Kaolinite can act as an immobilizer preventing the formation of TiO_2 particle aggregates in NaOH solution and hence increasing the effective surface area and photocatalytic efficiency [18]. Catalyst improvement via immobilization might be also owed to the force field between the support and TiO_2 particles that inhibits the recombination of electron–hole pairs [19]. Additionally, the presence of kaolinite can change the acidobasic properties of the catalyst surface and hinders the crystallite growing as implies from calculated *Lc* values for Degussa P25 and KATI66 (Table 1). According to previous works [20–24], the crystallite size is an important parameter for photocatalytic efficiency. The optimal value of TiO_2 crystallite size for CO_2 photocatalytic reduction was found to be 14 nm. This value corresponds to the highest yields of the main CO_2 photocatalytic reduction products [20]. This is in agreement with results obtained in this work where the photoreactivity of TiO_2 increases as the particle size is decreased from 26 nm to 18 nm.

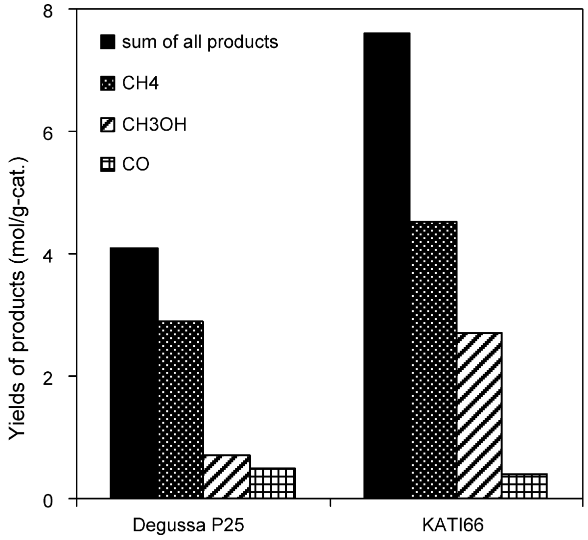

Fig. 5. Dependence of the CO_2 photocatalytic reduction product yields over KATI66 and Degussa P25 catalysts. *Conditions*: 24 h of irradiation time, 8 W Hg lamp, CO_2 pressure at carbonation of 110 kPa, 100 ml of 0.2 M NaOH, catalyst concentration of 1 g l^{-1}, pH 7.

4. Conclusion

The photocatalytic properties of the prepared kaolinite/TiO_2 catalyst were evaluated by photocatalytic reduction of CO_2. A slight decrease of specific surface area was observed for the kaolinite-modified sample compared to the Degussa P25 commercial TiO_2 catalyst. The observed improvement of photocatalytic activity of kaolinite/TiO_2 compared to the commercial TiO_2 catalyst can be caused by (i) higher effective surface area due to lower agglomeration in kaolinite/TiO_2 suspension, (ii) lower recombination rate of electron–hole pairs, (iii) change of the acidobasic properties of the catalyst surface and (iv) lower crystallite size as the yields of the CO_2 photocatalytic reduction products increase with the decrease of crystallite size. With respect to obtained results, the KATI66 composite represents a valuable photocatalyst for the photodegradation of CO_2.

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