

Ageing of Photocatalytic Materials: Investigation, Assessment and Possible Solving

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The stability of composite materials (TiO₂-film deposited on a kaolinite and montmorillonite matrix) in time was investigated. The obtained results showed that the adsorption activity (capacity and specific area) decreased in comparison with the results of 2011. It was found that the samples in which the content of titanium dioxide is not more than 100-120 mg/g, characterized by the highest stability. As regards the influence of UV-radiation, the results demonstrate that the sensitivity to UV radiation for kaolinite matrix materials increases as the estimated content of TiO₂ up to 100 mg/g in presence of UV-irradiation, and up to 150 mg/g - in the presence of pre-activation, whereas the influence of ultraviolet on montmorillonite is noticeably lower.

1. Introduction

Indoor air pollutants strongly affect human health, comfort and productivity. Volatile organic compounds (VOCs) are among the most abundant chemical pollutants in the indoor air that we breathe. Some of these compounds are associated with sick building syndrome (SBS) including mucous membrane irritation, headache and fatigue; others are known carcinogens. Millions of people are currently suffering from the consequences of poor indoor air quality. (Wang et al., 2007)

Among others, photocatalytic oxidation (PCO) processes in gas phase is an innovative and promising approach due to its prospective applications in the environment purification. Titanium dioxide is one of the best known and most used materials with photocatalytic properties, by such qualities as photochemical stability, high activity under natural light or artificial light, relatively low cost, availability, absence of chemical and biological toxicity, redox properties and the ability to prepare materials with various morphology. (Liu et al., 2011a; Kubacka et al., 2012a; Liu et al., 2012b) However, most methods allow to produce only powdered photocatalyst, the use of which is limited in chemical technology. In this regard, the focus is on the creation of nanostructured coatings of TiO₂ and selecting an optimal matrix for photocatalyst, which will be chemically and photochemically stable, and capable to capture of particles of the TiO₂. That is why the selecting an optimal carrier for photocatalyst material is the one of the most promising directions in the study of this technology.

This paper describes the results of studies of the stability of photocatalytic materials deposited on a clay matrix. The objective was to study the effect of different types of clays on the stability of the material and to identify the best estimated amount deposited titanium dioxide.

2. Experimental

This work is performed within the scientific direction of the Department Materials, Environmental Sciences and Urban Planning, UNIVPM. The scientific research base was laid during the project "Cataclean" (2009-2011, UNIVPM-LSTU). Technology of deposition titanium dioxide film has been proposed as part of the project, and the ability to photocatalytic decomposition of organic pollutants has been proven. (Prokofieva et al., 2012c). Investigation was carried out on the analyses of adsorption isotherms of water vapour and studying the kinetics of methyl ethyl ketone adsorption (including the investigation of UV-irradiation impact).

2.1 Materials

In order of "Cataclean" project, several samples of photoactive materials were obtained by the method of high-temperature hydrolysis of titanium precursors with the formation of titanium dioxide and its deposition on the matrix. For the preparation of the precursor its industrial titanium (the grade is VT1-00) have been used, while as a carrier materials montmorillonite (Montmorillonite K-10, Fluka AG) and kaolinite (Industria Chimica Carlo Laviosa) have been selected. Before the treatment, the matrix phase of size < 10 microns was separated from the matrix by sedimentation method. For varying of the titanium dioxide content the samples with different ratio clay/reaction solution were prepared (see Table 1). After preparation, the content of was determined by atomic emission spectroscopy analyses, the results of which revealed that the actual content is much lower, as it represented on the Table 2. A possible cause is the loss occurring during grinding of the material. In order to study the stability of the adsorbents obtained in 2011, and their adsorption properties were retested three years later.

Table 1: Samples 2011 (project "Cataclean")

| Matrix | Conditions of sample preparation | | | | Sample ID |
|-----------------|----------------------------------|---|---------------------------|------------------|-----------|
| | Material weight, g | The volume of the reaction solution, ml | Estimated content, mg / g | | |
| | | | Titan | Titanium dioxide | |
| Kaolinite | 2 | 10 | 171.5 | 286.4 | K2 |
| | 4 | 10 | 85.8 | 143.2 | K4 |
| | 6 | 10 | 57.2 | 95.5 | K6 |
| Montmorillonite | 1 | 7 | 214.2 | 357.7 | M1 |
| | 2 | 7 | 107.1 | 178.9 | M2 |
| | 3 | 7 | 71.4 | 119.2 | M3 |

In order to study the adsorption properties of the materials, the following data were obtained and analyzed in comparison with the results of 2011: of water vapor adsorption isotherms, the kinetics of methyl ethyl ketone (MEK) adsorption and influence of irradiation activated adsorption.

2.2 The designing and analysis of water vapor adsorption isotherm

Isotherms of water vapor adsorption were designed by gravimetric method. Desiccator (2 l) was placed an air thermostat at 25°C. At the bottom of the desiccator was a ceramic cup, into which was added 50 ml of aqueous solution of sulfuric acid at various concentrations (for regulation of relative pressure). First, the solutions were changed from strongest to more diluted (adsorption phase), then (after achievement of $p/p_s=1$ with distilled water) - on the contrary. Weight of the sample regularly measure that allowed to define the capacity and design of the isotherms.

2.3 The investigation of the kinetics of methyl ethyl ketone adsorption

The sample of each material (0.2 g) was placed in the sealed vial (43.6 ml), equipped with a one-way permeable membrane and magnetic stirrer to stir the air inside. MEK was used as modeling pollutant because of its stability and resistance to decomposition, as well as because its high odour threshold value (OTV) of $0.75 \times 10^{-3} \text{ mg L}^{-1}$ (250 ppb) and a threshold limit value (TLV) of 0.6 mg L^{-1} (200 ppm). The smell of this compound is easy to detect, while the sweet odor of MEK is not disagreeable, mixed with other odorants an unpleasant odour can be formed (Rappert et al., 2005).

During the experiment, the probe of methyl ethyl ketone (1 μl) was inject in vial. The sampling of air was implemented in every 2-3 min. The duration of each experiment was 10-30 minutes.

2.4 Study of irradiation activated adsorption

Samples of materials (1 g) were placed in a desiccator (16 l), equipped with a fan to stir the inner air. Methyl ethyl ketone (100 μl) was used as a modeling pollutant. The analysis was implemented by gas chromatograph GC 8000, the duration of each experiment was 120 minutes, depending on the its capabilities. The sampling of probes of air from the desiccator (10 μl) carried out every 10-15 minutes.

Testing was carried out in three phases: the analysis of samples without UV (for comparison) and under UV-irradiation. Besides that, promising kaolinite-based materials were additionally examined with an UV pre-activation (for a period of 2 to 8 hours). For UV-radiation tests the ULTRA-VITALUX lamp was used.

The results of first 20-30 min are ignoring because of huge volume of desiccator in compared with pollutant's volume (this time was spent to equalization of the concentration). That is why the estimated value is the slope of the regression line.

3. Results and discussion

3.1 Analyses of water vapor sorption isotherms

It has been found that the adsorption capacity remained almost unchanged compared with the results of 2011. Based on the isotherms the relationship between stability of adsorption capacity and the amount of the component were investigated (see Figure 1). It has been established, that thermo-acid treatment and titanium dioxide deposition has a great influence the activity of the samples, especially for kaolinite-based.

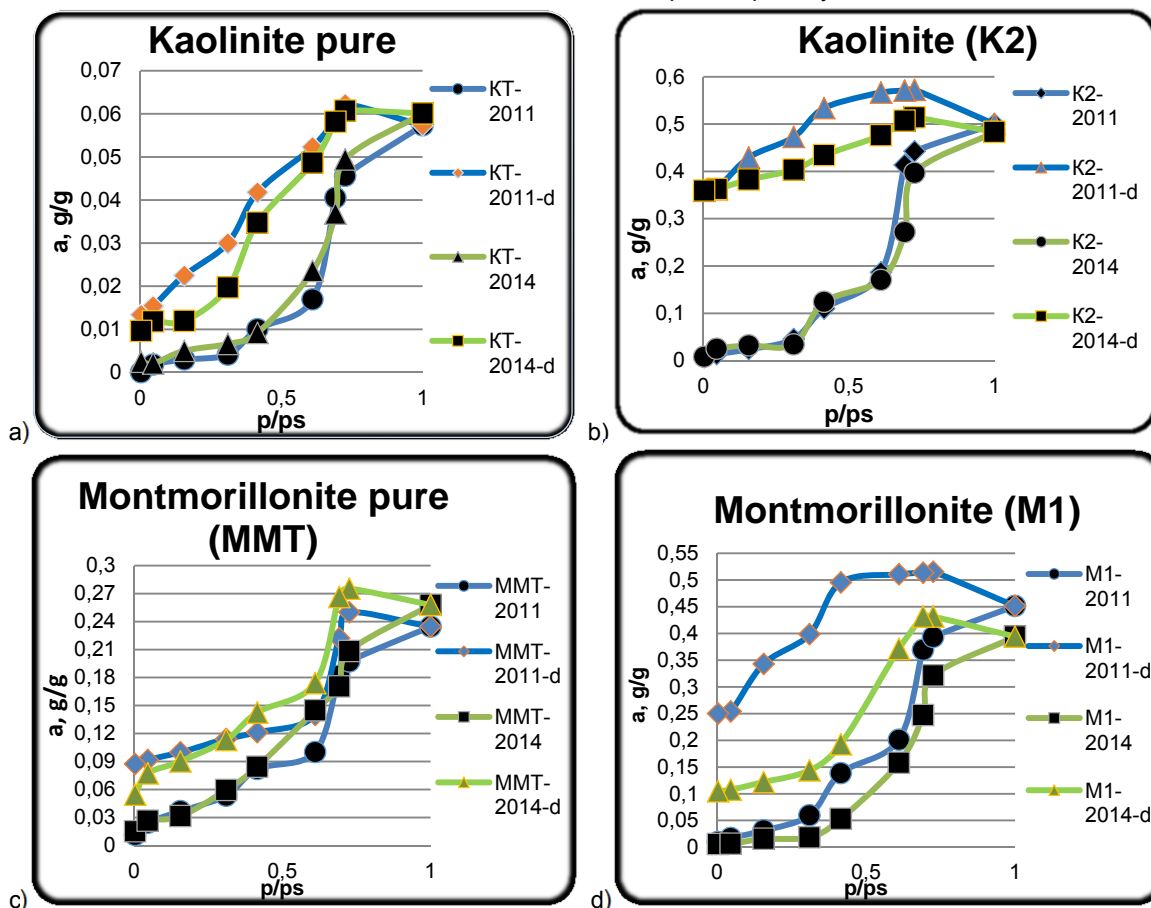


Figure 1: Examples of adsorption and desorption isotherms of water vapor for kaolinite-based materials of 2011 and 2014: a, c) samples of pure kaolinite and montmorillonite, b, d) samples with deposited TiO_2 . After processing of data, obtained by analyzing of the isotherms, it was confirmed that kaolinite based samples showed better stability, than montmorillonite-based. However, it is worth to note the influence of deposited titanium dioxide (see Figure 2).

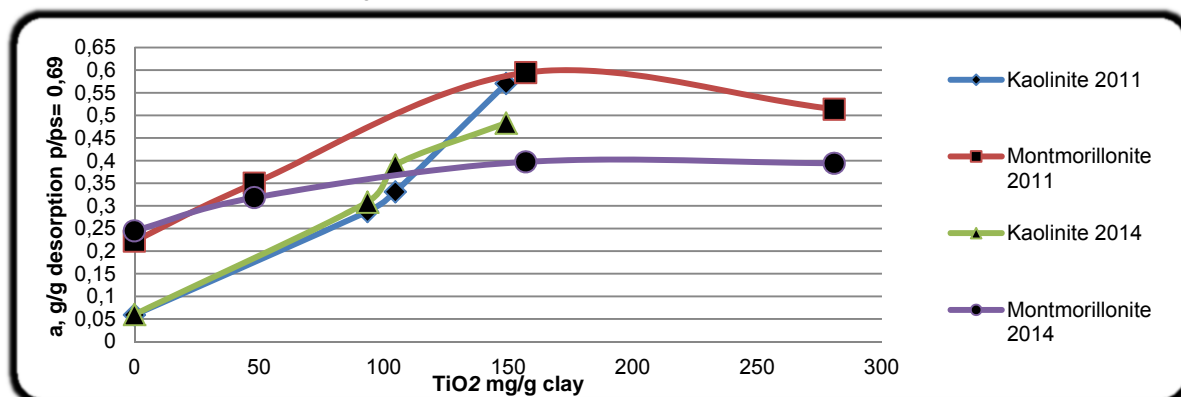


Figure 2: Effect of TiO_2 -content on the stability of adsorptive properties

Thus, the objectives were defined:

- 1) Investigation the properties of clay matrix,
- 2) Identification of the impact of TiO₂-content.

3.2 Comparison of the structural characteristics of the samples

The adsorption properties are largely determined by such parameters of supramolecular structures as specific surface area, the volume of micro- and mesoporous. These parameters were calculated for adsorption isotherm of water vapor. The results are shown in Table 2

Table 2: Specific surface area and porous structure of the samples

| Samples | TiO ₂ contents mg/g | a _{max} mol/g | S _{sp} m ² /g | V micro cm ³ /g | V meso cm ³ /g | V lim cm ³ /g |
|----------------------|-----------------------------------|---------------------------|--------------------------------------|-------------------------------|------------------------------|-----------------------------|
| Results -2011 | | | | | | |
| K2 | 149.2 | 0.00180 | 139.0 | 0.0325 | 0.498 | 0.500 |
| K4 | 104.7 | 0.00174 | 133.9 | 0.0313 | 0.320 | 0.322 |
| K6 | 93,5 | 0.00173 | 133.7 | 0.0312 | 0.279 | 0.281 |
| KT | 0 | 0.00017 | 13.2 | 0.0031 | 0.057 | 0.057 |
| M1 | 280.9 | 0.00235 | 181.3 | 0.0424 | 0.449 | 0.451 |
| M2 | 157,1 | 0.00243 | 187.5 | 0.0438 | 0.505 | 0.508 |
| M3 | 48.1 | 0.00229 | 176.4 | 0.0412 | 0.345 | 0.348 |
| MMT | 0 | 0.00208 | 160.5 | 0.0375 | 0.232 | 0.235 |
| Results -2014 | | | | | | |
| K2 | 149.2 | 0.00134 | 103.0 | 0.0241 | 0.482 | 0.482 |
| K4 | 104.7 | 0.00123 | 94.4 | 0.0221 | 0.389 | 0.389 |
| K6 | 93,5 | 0.00066 | 50.6 | 0.0118 | 0.308 | 0.308 |
| KT | 0 | 0.00025 | 19.6 | 0.0046 | 0.060 | 0.060 |
| M1 | 280,9 | 0.00082 | 62.8 | 0.0147 | 0.393 | 0.393 |
| M2 | 157,1 | 0.00157 | 121.0 | 0.0283 | 0.369 | 0.397 |
| M3 | 48,1 | 0.00145 | 111.9 | 0.0261 | 0.292 | 0.318 |
| MMT | 0 | 0.00225 | 173.1 | 0.0404 | 0.217 | 0.258 |

After 3 years, limited adsorption volume (V lim) and volume of mesoporous (V meso) virtually have not change over time, while volume of microporous and specific surface area have been decreased significantly, in 1.35-2.90 times. However, for kaolinite-based materials they are still higher than original parameters of "pure" clay matrix. It worth to note, that the characteristics kaolinite increased six times after the treatment, while for montmorillonite the same parameters increased less than 1.2 times. Thereby kaolinite reached comparable values and showed several advantages as matrix over time, despite its flaws.

3.3 Investigation of the kinetics of methyl ethyl ketone adsorption

All the samples were characterized by a decrease of sorption capacity toward MEK, but, as it represented on the Figure 3, there is an inverse relationship between the amounts deposited titanium dioxide and stability of the material.

The using kinetic equation of the second allow order (see Eq1) to calculate the limited sorption volume and rate constant of adsorption (Kolpakova et al., 2011b)

$$\frac{\partial^{a_t/a_{max}}}{\partial t} = k_{ads} \left(1 - a_t/a_{max}\right) \quad (1)$$

Where: a_t - current capacity, a_{max} - maximum sorption capacity, k_{ads} - adsorption rate constant

The results were demonstrated in Table 3.

There is an inverse relationship between the amount deposited titanium dioxide and stability of the material.

Table 3: Limited sorption volume and rate constant of adsorption

| Sample | a_{\max} , mg/g | | k_{ads} , mg/(g*min) | |
|--------|-------------------|------|-------------------------------|-------|
| | 2011 | 2014 | 2011 | 2014 |
| KT | 3.64 | 3.27 | 1.12 | 1.38 |
| K6 | 3.04 | 4.10 | 3.67 | 0.81 |
| K4 | 3.79 | 4.13 | 7.46 | 1.05 |
| K2 | 3.59 | 3.22 | 5.25 | 0.23 |
| MMT | 4.02 | 3.58 | 23.22 | 38.95 |
| M3 | 4.02 | 3.49 | 78.34 | 13.15 |
| M2 | 4.01 | 2.90 | 41.43 | 0.66 |
| M1 | 4.06 | 1.99 | 33.90 | 0.95 |

. According to the results given in Table 3, the maximum sorption capacity of the kaolinite in not only exceeds that of montmorillonite, but outperforming the values of 2011. This may indicate a change in the internal structure, as the internal diffusion to be the limiting step in given experimental conditions (intensive mixing, provides proactive external diffusion).

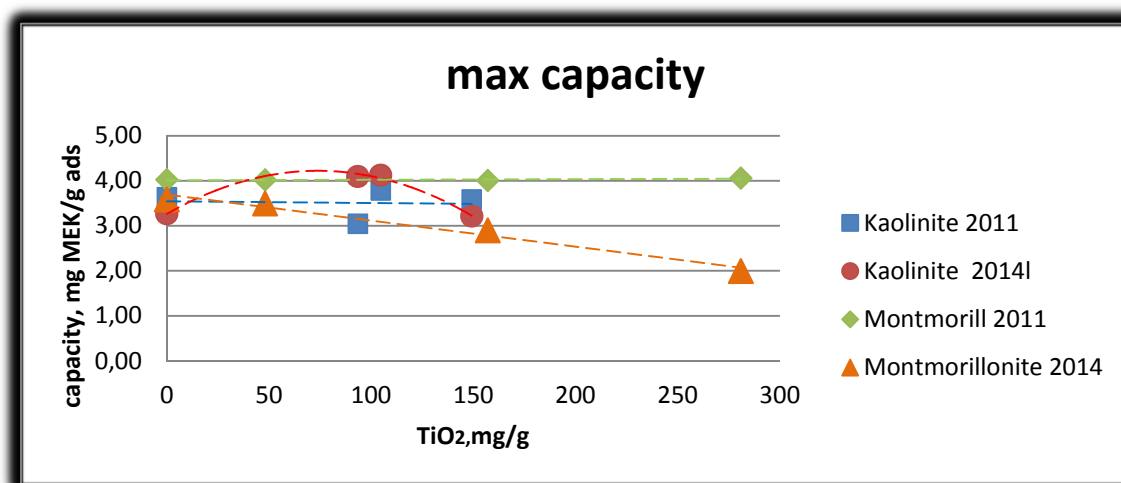


Figure 3: The exchange of sorption capacity towards MEK depending on the content of TiO₂ in sample

If the receiving material, the adsorption capacity directly correlates with the amount of composite material, after three years demonstrated the best results the samples in which the content of titanium dioxide is not more than 100-120 mg/g.

3.3 The effect of UV-radiation on the MEK degradation' kinetic

The experimental results also demonstrated the benefits of kaolinite as a matrix for composite materials, which were additionally investigated in order to determine the influence of the pre-activation. As mentioned above, the slope of the regression line was used to assess the activity of the samples (see Table 4).

According to this data, we conclude that the titanium dioxide responds to UV radiation, wherein the preliminary activation markedly increases the activity of the layer.

It is worth emphasizing that the slope of the concentration dependence is clearly non-linear and tends to flatten out.

The TiO₂-content is directly correlated with activity of material. However, best value for montmorillonite is reached at an estimated content of 150 mg/g, from which it can be concluded that the increase estimated amount is impractical.

Table 4: The value of the slope coefficients

| Sample | Slope, 10 ³ | | |
|--------|------------------------|---------|------------------|
| | No UV | UV | UV+activation UV |
| KT | -1.421 | -1.278 | |
| | -1.062 | | |
| K6 | -2.046 | -4.891 | -19.044 |
| K4 | -2.674 | -4.384 | -24.702 |
| K2 | -3.102 | -6.841 | -30.358 |
| | -2.534 | -6.289 | |
| | -2.572 | | |
| MMT | -1.576 | -1.993 | |
| MM3 | -3.759 | -6.068 | |
| MM2 | -2.682 | -11.673 | |
| MM1 | -2.277 | -8.356 | |

4. Conclusion

Adsorption characteristics of composite materials in both cases higher than those for "pure" matrices. It has been found, that kaolinite-based materials are more stable over time, than montmorillonite-based materials. More than that, adsorptive properties of kaolinite-based materials became comparable with montmorillonite, after the treatment, despite pure kaolinite matrix noticeably inferior to the analog.

It can be assumed, that the reason is the different chemical structure of matrixes, which provides the resistance of materials. Kaolinite more chemically inert by treatment with acid while montmorillonite belongs to the most unstable clay minerals and the acid treatment can disintegrate and pass into hydromica. However, the treatment of kaolin with sulfuric acid by heating is a known method of producing alumina, with a portion of alumina reacted to form aluminum sulphates. This topic is still in development.

Also, performance comparison showed that the calculated content of titanium dioxide should not exceed 100 - 120 mg/g. That may be due to the influence of the deposited titanium dioxide microporous structure.

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