

Ti-MODIFIED NON-SWELLING CLAY COMPOSITE: SYNTHESIS, CHARACTERISTICS AND POSSIBLE APPLICATION

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Introduction

In our previous work [1] we reported about synthesis of Ti – modified non-swelling clay based composites and their adsorption properties regarding Cr (VI). In current work we investigated the same samples by SEM and performed surface area measurements for all samples, these helped us to achieve more conclusions about influence of different parameters on the composites final characteristics. Furthermore, an adsorption experiment concerning cation Co^{2+} was performed to fully understand nature of surface active centres.

There is a high demand [2] for synthesis novel porous material derived from cheap and available chemicals with improved surface properties is increasing over the last 10 years. Those materials are important for such areas as catalyst and adsorption [3].

Let us remind that in previous work we reported about non-swelling clay (muscovite) modification by TiO_2 . There were used different approaches to the synthesis, particularly¹:

- changing solvent for synthesis from distilled to mineral water (containing mainly Ca^{2+} and Mg^{2+} chlorides/sulphates/carbonates with ratio 1:3:6; the metals ratio $\text{Ca}^{2+}/\text{Mg}^{2+} \sim 2$);
- adding relatively severe heat treatment – evaporation step.

The full synthesis scheme is displayed at figure 1 with marks for the samples explanations.

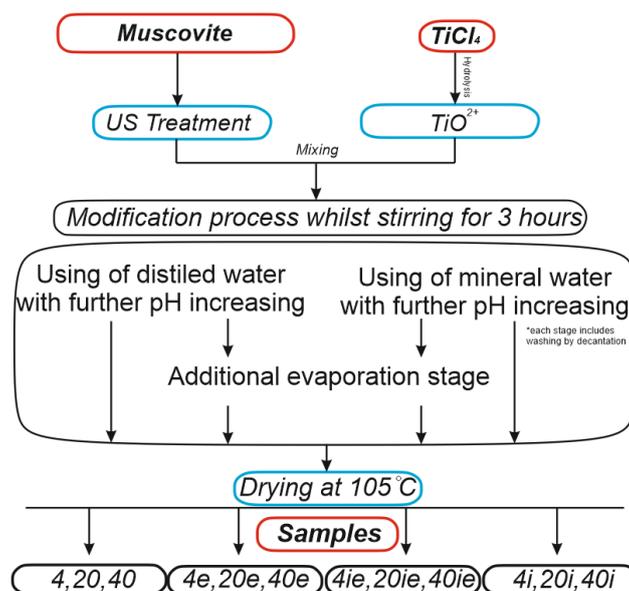


Fig. 1: Synthesis scheme [1]

Results

Surface Area Measurements

We performed surface area measurement by the means of N_2 -adsorption. Technique of N_2 adsorption with Quantachrome NOVA 1200e was a standard [4]. Results are displayed in Table 1.

Table 1: Surface Area Measurements with N_2

Sample	MT	4	20	40	4e	20e	40e	4i	40i	4ie	40ie
SA, m^2/g	263	290	315	230	219	254	238	286	259	308	273

The surface area of all modified clay samples with low titanium concentration has been increased, except *4e* sample. The *4e* demonstrates the lowest surface area among the samples and whole *e*-set show low surface area values.

We consider, this phenomenon is attributed to influence of evaporation step improved the TiO_2 particles aggregation process in time. While, the same behaviour does not work with *ie*-set of samples, however these also were additionally evaporated. This can be a result of affection of positively-charged ions in mineral water partially compensated negative charge of clay lamellar resulting in almost neutral surface state. Consequently, in the way of surface area measurement description the aggregation processes didn't affect *ie*-samples significantly. Moreover, the *4ie* has the largest surface area among other composites.

For all samples modified with 40 mmol of titanium amount there is detected a diminish of surface area values in comparison with their sets. This phenomenon links to TiO_2 grains growing processes to bigger size with higher metal concentration is more preferable for the system instead of to penetrate the interlayer space. These results are convenient with XRD analysis¹ where amount of anatase phase had become detectable for *40*-set of composites.

SEM

The experiment was carried out on JEOL JSM-5500 LV apparatus equipped with analyser IXRF Systems and detector Gresham Sirius 10 (Joel Inc., USA).

The images for *4* and *4i* samples are shown at figure 2 and revealed difference in the appearance of the composites depends on chosen solvent.

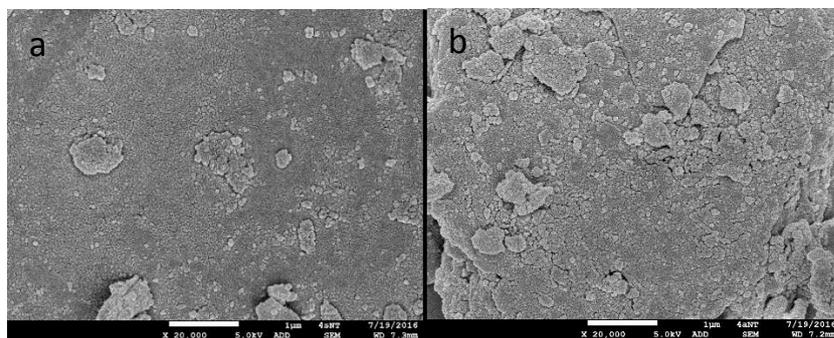


Fig. 2: SEM images of a) *4* and b) *4i*

Firstly, it should be noted that both samples are covered by layer of TiO_2 . This means that 4 mmol of $Ti/1$ g of muscovite is enough to cover almost all visible surface. However, regardless of the last fact, the clay platelets are more recognisable for *4i*. We attributed this phenomenon to the fact cations TiO^{2+} during

the modification process were partially bonded with anions in mineral water as a solvent, resulting in decrease of TiO₂ yield on the surface.

The same effect is properly observed for 40e and 40ie (figure 3), where clay platelets are clearly seen for 40ie at the figure 3b.

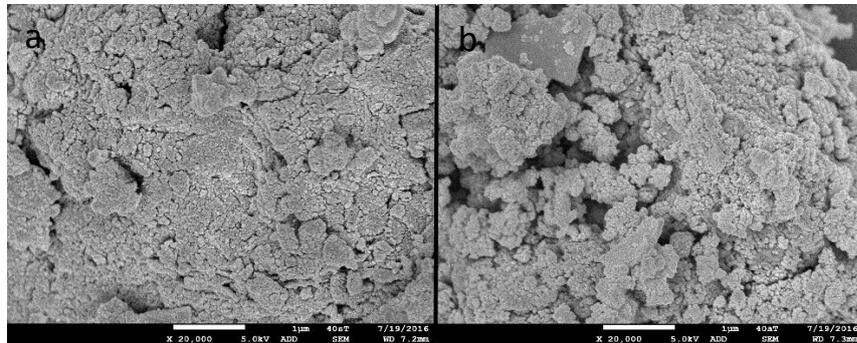


Fig. 3: SEM images of a) 40e and b) 40ie

The difference in TiO₂ particles size is properly revealed for 4 and 4i composites with bigger grains for 4i (figure 4). There is in average ~ 30 nm in size for TiO₂ grains for 4i and ~25 nm in average for 4. However, it should be noted that size distribution parameter is much more variable for 4.

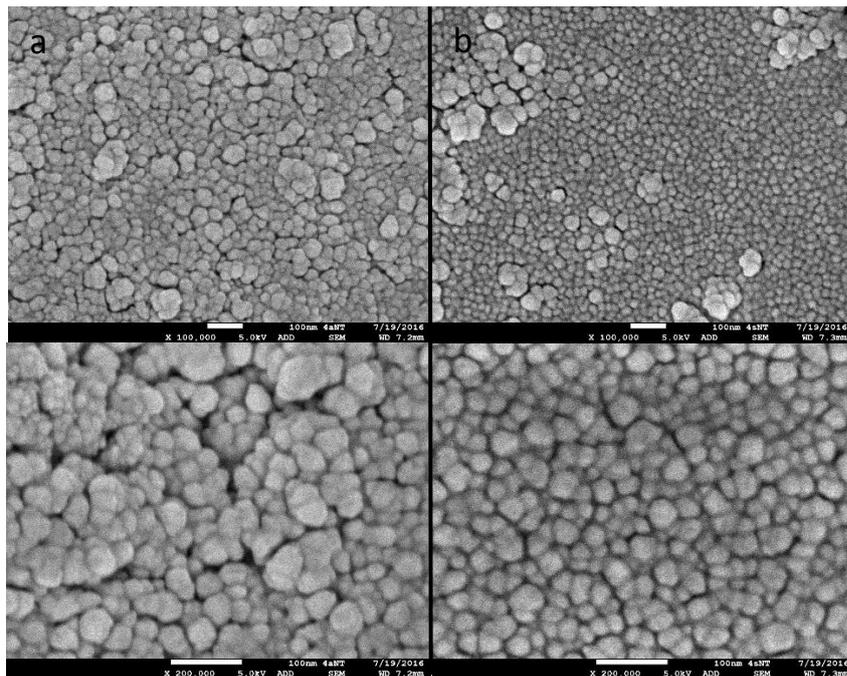


Fig. 4: Difference in TiO₂ grains size for a) 4i and b) 4

Adsorption Expertise

It was performed adsorption of Co²⁺ cations by the mean of the composites to understand their surface properties. As well as to obtain a ratio between active centres those are able to adsorb positively/negatively charged ions using data derived in previous work [1].

The method we used in the work is known: 0.1 g of the sample was weighted accurately up to 4th number after point and added to CoCl₂ solution with fixed

concentration and pH. The measured concentration for Co (II) were at 9 and 33 mmol/L; the chosen pH: 4 and 6. The contact time was 4 hours, whilst shaking. The residual concentration was measured by the means of atomic-adsorption analysis in air flame.

4 samples were examined in adsorption experiment relative to removing of Co^{2+} compounds from aqueous solutions. The results of adsorption experiment are demonstrated on the figure 5a and updated results from previous work [1] to compare amount active different nature centres are shown on the figure 5b.

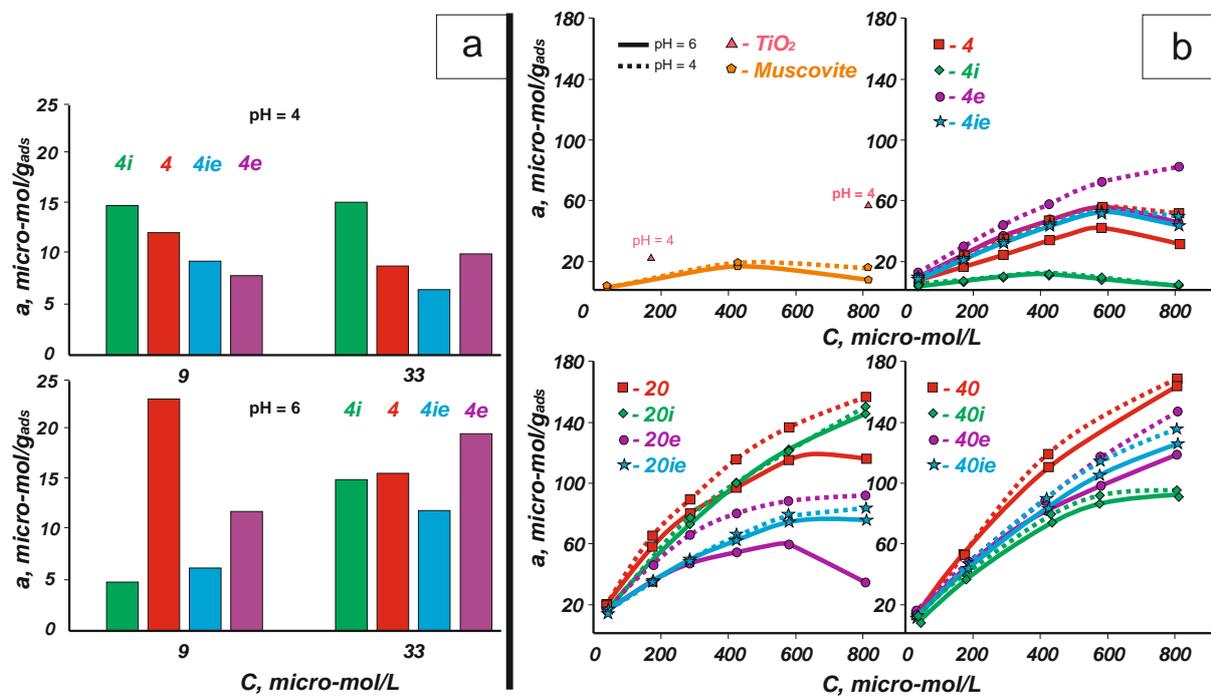


Fig. 5: Adsorption experiment results

As it was seen from the experiment the adsorption of cations is very low that means miniscule amount of active centres those are able to adsorb positively charged shapes.

Before the experiment it was assumed that if Cr (VI) anions adsorption on the 4i sample is low, the reaction of the adsorbent with positively-charged metal should reveal higher efficiency. This assumption was failed. It seems to be, that ions from the mineral water solvent captured available active centres and Co^{2+} adsorption process depends on cobalt ions affinity to surface in comparison with ions those already occupied the active centre.

In general, it is very difficult to work with such small adsorption values and compare the results and their efficiency because experimental inaccuracy leads the dance. However, this can be concluded that the synthesised composites contain mainly active centres those are able to adsorb anions species of heavy metals.

Conclusions

All in all, in current work we performed further investigation of Ti-modified muscovite by the means of Surface Area Measurements, SEM and Co^{2+} adsorption. High amount of the modified (40 mmol of Ti/1 g of muscovite) leads to TiO_2 particles aggregation which reduce surface area of the 40-set samples. The varying of the

synthesis solvent to mineral water resulting on unevenness TiO₂ particles distribution on the surface and their increased sized in comparison with samples derived in distilled water. By the means of adsorption expertise on Co²⁺ it was shown, that amount of active centres with ability to adsorb cations species is miniscule.

Acknowledgements

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References

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