Si/Zr modified clays prepared by various procedures: preparation and characterization

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INTRODUCTION

Clay minerals are a good choice as a precursor for porous materials due to their environmental friendliness, low price, high selectivity, reusability, and high chemical and mechanical stability. Silica modified clay also has many applications due to its hydrophobicity, pore volume, specific surface area and high thermal stability. Clay with a columnar structure containing only silicon, however, does not have a variety of functions. The integration of other atoms or organic functional groups into silica-modified clay structures has proven to be a suitable way to expand its applications. It has been shown that the incorporation of zirconium can lead to a significant increase in the acidity of the primary clay, producing a Brönsted-type acidity and suitable samples for catalytic applications.

Therefore, the simultaneous modification of clay with silica and zirconium increases porosity and enhances catalytic and adsorptive properties. The loading of zirconium particles in the clay structure with SiO_2 columns can lead to the closure of pores and active sites and greatly reduce the specific surface area. Depending on the application, the loading of zirconium in the clay structure is also very important. Therefore, it is very important and necessary to find a suitable method for doping metals on silica modified clay without placing metals outside the structure. In this study, the primary clay is modified with Si and Zr in three different ways and the structure of the samples is investigated.

OBJECTIVES

The object of this study is to modify clay with silica and zirconium in three different ways to investigate the structure of the samples.

MATERIALS & METHODS

The raw clay was provided as a raw material.

Tetraethyl orthosilicate (TEOS), ethanol, cationic surfactant hexadecyltrimethylammonium bromide (HDTMA), ammonia solution (25%) and zirconium salt ($ZrOCl_2.8H_2O$) were provided from Merck.

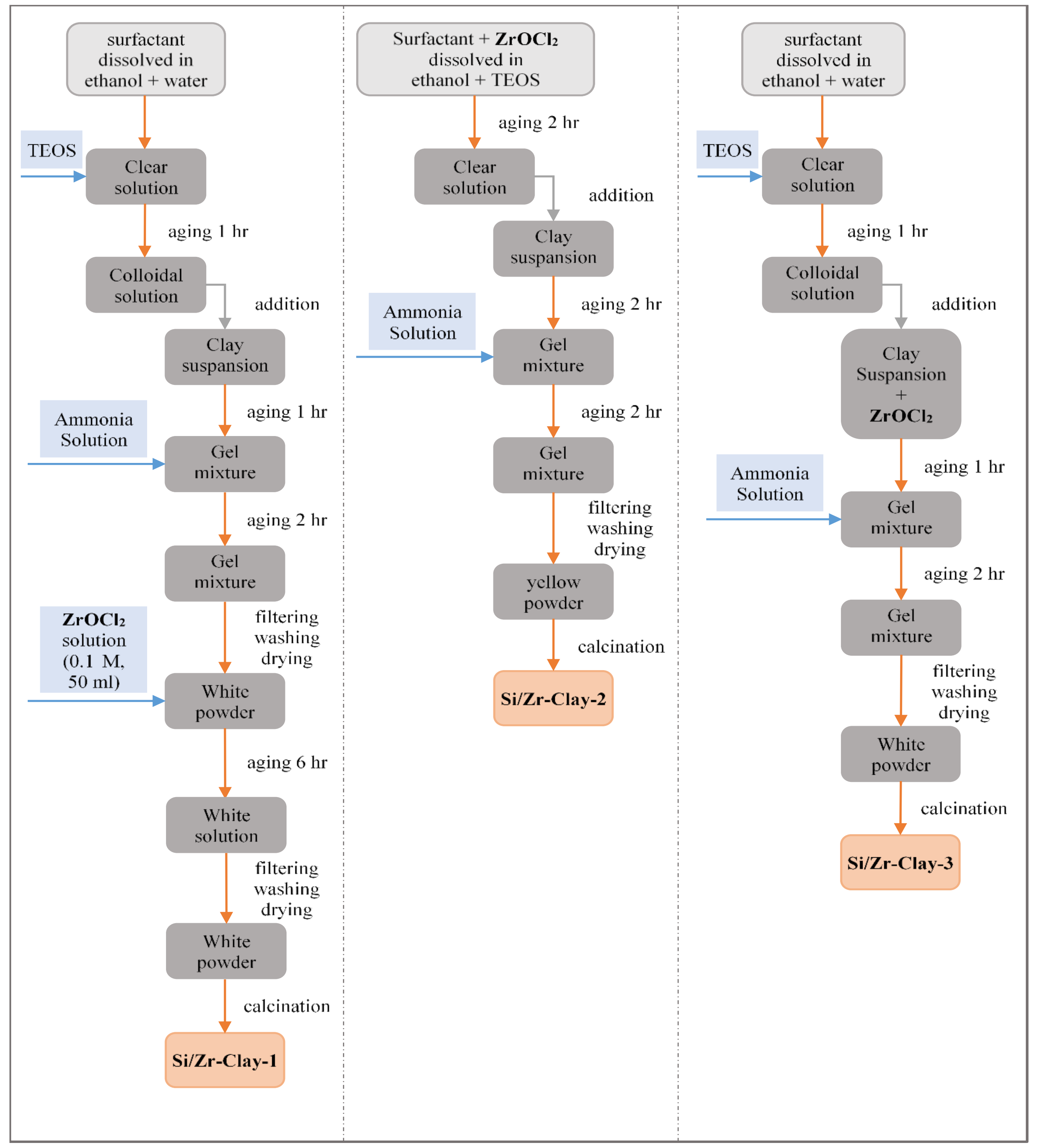
Three different types of modified clays containing silica and zirconia pillars were produced according to the following methods:

Method 1: Adding zirconium after the preparation of silica modified clay before calcination [1].

Method 2: Adding zirconium during the process of preparation with silica (by adding Zr to Si solution) [2].

Method 3: Adding zirconium during the process of preparation with silica (by adding to clay suspension) [3].

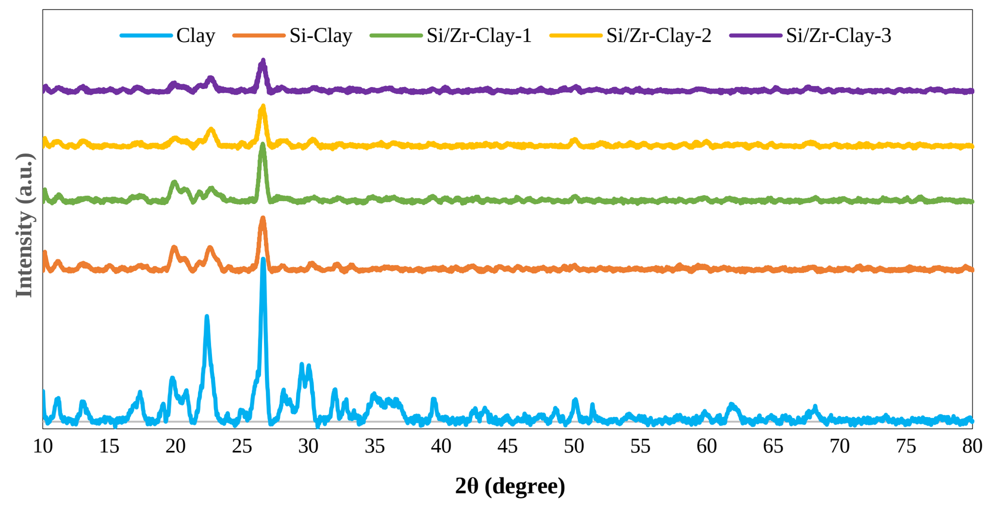
For all synthesis methods, 3% clay suspension was prepared from sodium clay and distilled water. The mass ratio (w/w) of zirconium salt ($ZrOCl_2.8H_2O$) to sodium saturated clay is 1.6 for all methods. The opposite figure shows a schematic diagram of the Si/Zr-Clay synthesis steps in the above three methods.



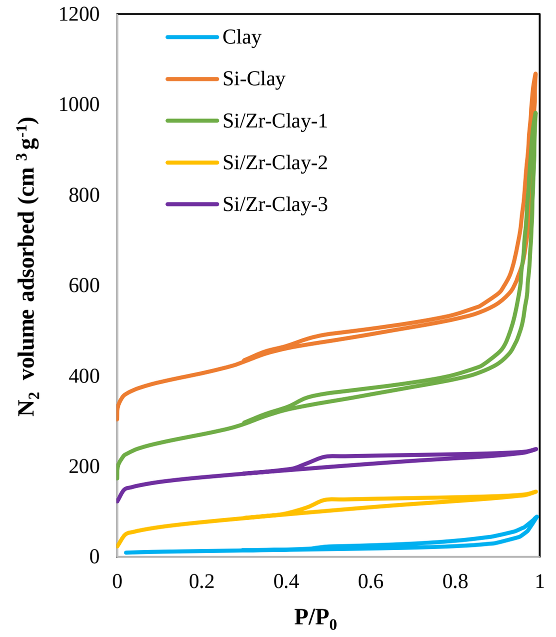
RESULTS

XRF analysis performed to determine the chemical composition of the synthesized samples. The weight percentage of SiO_2 increased from 74.6 to 93.6%, indicating the successful formation of Si-containing pillars in the sample Si-Clay. Each modification method led to the addition of different amounts of ZrO_2 to the structure of the synthesized samples. In the third method, the highest amount of Zr was generated in the Si/Zr-Clay structure.

The figure below shows the X-ray diffraction pattern of all synthesized samples in comparison with the original clay. The prominent peaks in the XRD pattern of the sample Si-Clay are observed at the same positions; therefore, the layered clay structure is preserved during the modification. However, the intensity of all peaks has decreased, which means the reduced crystallinity compared to the clay, and it is related to the synthesis of amorphous SiO_2 particles. The curvatures and peaks in the diffraction pattern of the sample Si-Clay and the samples containing zirconium are similar. It also indicates the preservation of the Si-Clay layered structure after the addition of Zr. Also, a detectable peak of the crystalline ZrO_2 phase is not observed in the Si/Zr-Clay samples due to the low degree of crystallinity of the phase. With the increasing amount of ZrO_2 in the synthesized samples, the peak intensities decrease relatively, corresponding to a decrease in the degree of crystallinity after the addition of zirconium.

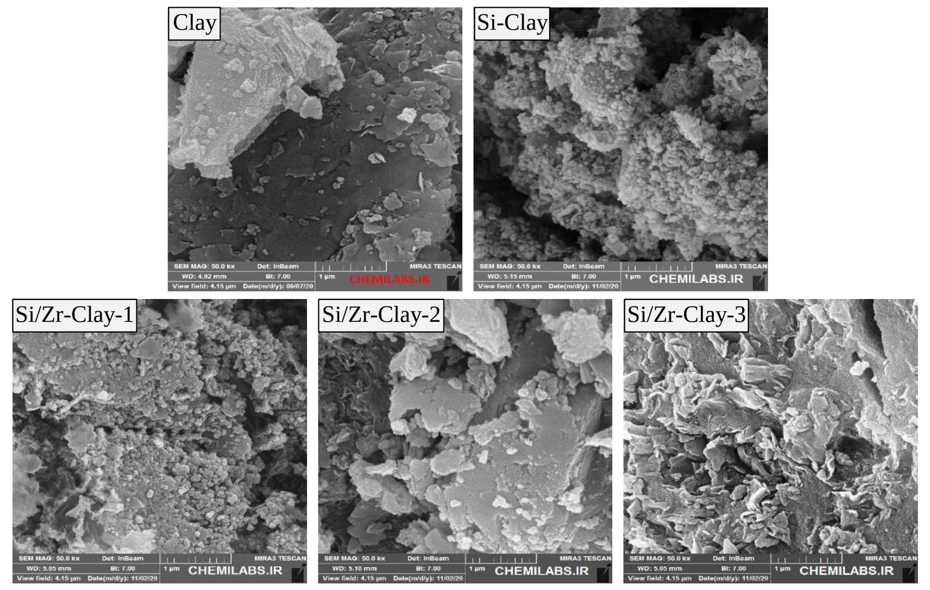


The figure below shows the N_2 adsorption/desorption isotherms for the primary and modified clay samples. All the isotherms show a hysteresis loop, which shows mesopores' presence in the clays' structure, with the highest percentage of micropores for Si-Clay and Si/Zr-Clay-1. Si/Zr-Clay-1 with the lowest percentage of Zr (2.1%) has the most similar structure and adsorption-desorption curve to Si-Clay. Increasing the percentage of Zr in combined samples (Si/Zr-Clay-2 and Si/Zr-Clay-3) leads to adsorption-desorption curves more similar to the raw clay. The table below shows the specific surface area, total pore volume and average pore size of the samples, and the weight percentage of zirconium oxide. With increasing zirconia loading, the average pore size decreases due to the extensive pore blocking, specific surface area, and total pore volume also decrease due to the external species of Zr.

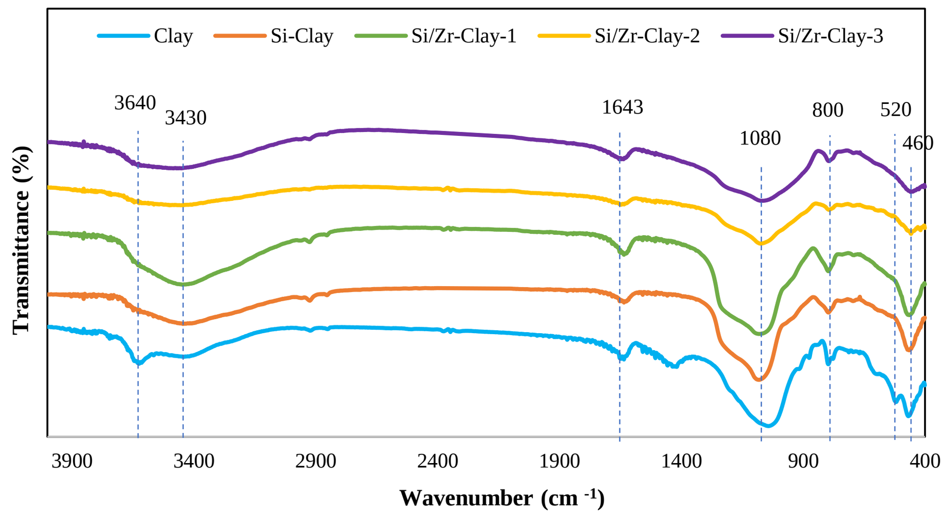


Sample	S_{BET} (m^2/g)	Pore size (nm)	Pore volume (cm^3/g)	Zr content (wt %)
Clay	45	11.2	0.13	0
Si-Clay	477	10.2	1.22	0
Si/Zr-Clay-1	459	11.0	1.26	2.1
Si/Zr-Clay-2	276	3.2	0.22	39.1
Si/Zr-Clay-3	274	3.1	0.21	44.6

The SEM images of the synthesized samples are shown in the figure below. Compared with the smooth texture of the raw clay, Si-Clay has a more heterogeneous surface containing a more significant number of amorphous SiO_2 particles. Si/Zr-Clay-1 does not differ from the Si-Clay due to the low percentage of Zr used. However, increasing the percentage of zirconium oxide on the surface samples Si/Zr-Clay-2 and Si/Zr-Clay-3 is associated with more clogged surface particles and larger external particles.



FTIR analysis of the synthesized samples also showed that the original structure of the clay was preserved after the modification process with silica and zirconium.



CONCLUSIONS

Modified clay with silica and zirconium (Si/Zr-Clay) was synthesized using surfactant as a template in three different ways. In all three methods, the same ratio of $ZrOCl_2$ salt/raw clay was applied. XRF analysis showed that the sample obtained by the third method (zirconia addition during the pillaring process) contained higher zirconia content than the other two methods and created a specific surface area and smaller pores by placing it in the Si-Clay interlayer space. The results of N_2 adsorption/desorption analysis confirmed the microporous and mesoporous structure of all synthesized samples, with the highest surface area for S-Clay and Si/Zr-Clay-1. Amorphous SiO_2 and ZrO_2 particles were observed by XRD and SEM analysis. The results of FTIR analysis show the preservation of the original structure of the original clay after the modification process. Samples containing Si columns and ZrO_2 particles can be applied as suitable materials for catalytic and adsorption applications due to their specific surface area and high porosity, thermal and mechanical stability, and high acidity.

REFERENCES

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