PHASE TRANSFORMATION OF ION-EXCHANGED TITANO SILICATE MATERIAL

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ABSTRACT

The phase transformation and thermal stability of Co^{2+} and Cu^{2+}-exchanged titanium silicate ETS-10 material, prepared by using cobalt (II) and copper (II) nitrate solution, and subsequent calcinations at different temperatures and cooled down to room temperature, were investigated by X-ray Powder Diffraction (XRD), Scanning Electronic Microscope (SEM), Elemental and Thermal Analysis. It found that the metal (II) exchanged ETS-10 material exhibits a high thermal stability at 723K.

The microspore system of Co^{2+}-exchanged ETS-10 material changes into Narsarsukite ($NaM^{2+}TiOSi4O10$) structure upon thermal treatment at 1023K, a further structure transformation into Rutile (TiO_2), Cobalt oxide (CoO), and Tridymite (SiO_2) materials upon heating the sample at 1223K.

The formation of Narsarsukite, Rutile and Tenorite (CuO) occurs when the sample of Cu^{2+}-exchanged titanium silicate ETS-10 heated at 1023K. Phase transformation into Rutile, Tenorite and Tridymite materials upon heating Cu^{2+}-exchanged ETS-10 material at 1223K.

Keywords—Titanium Silicate, ETS-10, Ion exchange, Phase transformation, XRD.

1. INTRODUCTION

Microporous titanosilicate ETS-10 with an ideal composition $(NaK)_2Si_5TiO_{13}.xH_2O$ [1] is constituted from orthogonal TiO_6 octahedra chains and SiO_4 tetrahedra linked by corner-sharing oxygen atoms [2], forming a three-dimensional 12-membered ring network with a pore-opening size of about 0.8nm [3]. Each Ti atom in a six-coordinated state carries two negative charges, which balanced by exchangeable alkali cations, normally Na^+ and K^+ [1, 2]. Thus, ETS-10 has demonstrated to display unique adsorption properties towards divalent metal ions in aqueous solution [4-6]. Adsorption over zeolites has demonstrated to be a very efficient method because of many virtues of zeolites, such as high adsorption capacity, wide availability, low cost, and excellent stabilities [7-9].

Partially disordered crystals are attracting ever-increasing attention from researchers since their physical properties which controlled by intentional variation of the degree of disorder. This feature also makes them highly attractive for commercial use [10]. Microstructural characterization during phase transformation is an important tool for development from the present status of knowledge. In order to improve the properties of various products the production methods and properties still need to be studied [11]. Solid-state transitions initiated by random thermally induced fluctuations in the material that bring small ensembles of atoms or molecules to new positions corresponding to the product phase [12, 13].

Although crystallization and phase transformations are essential for many applications involving Titania, they have adverse effects on the stability of nano architectures, especially when they occur at elevated temperatures. At elevated temperatures, high surface area makes them prone to solid-state sintering, which leads to grain growth, densification, and eventually complete collapse of the structure [14-16]. Such processes more pronounced during phase transformations when bond breaking and enhanced mass transport take place, which can lead to grain growth and densification [17].

The thermal stability of the microporous titanosilicate ETS-4 [18] has investigated and it found that the material undergoes partial structural rearrangement at ca. 473K followed by complete amorphization at 773K. However, at 873K, a new-layered material formed, and then at 973K crystalline narsarsukite formed.

In preparing luminescent titanosilicates, the Er^{3+} ions introduced into the pores of ETS-10 via conventional ion-exchange techniques [19]. Er^{3+}-doped ETS-10 undergoing a phase transformation to synthetic narsarsukite [20] upon calcinations in air at temperatures of ca. 973 K. In the process, the Er^{3+} ions trapped in the narsarsukite lattice and the amount of erbium introduced into this material controlled by tuning the ion-exchange process [19].

This paper concerns a study of the phase transformation of $Co^{2+}$and Cu^{2+} ion exchanged ETS-10 structure during heating at different temperatures, using a combination of powder X-ray diffraction, scanning electron microscopy (SEM) and energy dispersive analysis by X-rays (EDAX).

2. EXPERIMENTAL

2.1. Reagents:

All Reagents were analytical grade and were used without further purification. The compositions of the starting materials as gels in terms of oxides were:

$3.7\ Na_2O : 0.95\ K_2O : TiO_2 : 5.7\ SiO_2 : 171\ H_2O$ ratios is for titanium silicate ETS-10.

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2. 2. Preparation of ETS-10:

10.0 g of sodium silicate (27.0 % SiO_2, 14 % Na_2O, and 59.0% H_2O) with 3.17g of distilled water stirred for ½ hour (denoted as solution A). Solution B was prepared by dissolving 1.33g of NaOH pellets in 9.33g of distilled water and slowly added with stirring to solution (A). 8.63g of $TiCl_3$ (15% solution in HCl) were added dropwise and stirring for ½ hour. 1.49g of potassium fluoride dehydrate was added to paste mixture and stirred for another one hour. About 0.2g of ETS-10 seeds were added to the resulting gel and kept stirring for one hour until the mixture became homogenous (pH is about 10.8) at room temperature, this gel was autoclaved under autogeneous pressure in a teflon-lined stainless steel autoclave for ten days at 453K. The resulting product cooled down to room temperature filtered, washed with distilled water and dried at room temperature.

2. 3. Preparation of metal exchanged titanosilicates:

A typical batch technique used for the introduction of Co^{2+} and Cu^{2+} ions into ETS-10, yielding a Ti/Co and Ti/Cu molar ratio of 1.4 and 1.25 respectively, (as ascertained by bulk, EDAX analysis) is as follow: 1.0 g of as-prepared ETS-10 was added to 250 ml of 0.05 M of the respective metal nitrate solution and then stirred for 24 h at 298K and pH value between 5.0 and 6.0. The solid filtered from suspension, then washed with deionized water and dried at room temperature. The resultant ETS-10 material was re-suspended in a fresh Co^{2+} and Cu^{2+} solution and the entire procedure repeated (second cycle), after which a third ion-exchange cycle was performed, exchangers were collected on filter paper and washed with deionized water following the final ion exchange; the samples were further washed and dried at room temperature.

The calcinations procedure carried out using thermal furnace for 4 h under flowing dry air at temperatures of up to 1223K.

2.4. Characterization methods:

Powder X-ray diffraction measurements carried out using Philips DW 1800 diffractometer interfaced to a PC and using X'Pert Philips operating software. The samples pressed into an aluminium holder for analysis. The powder patterns recorded for 2θ over the range of 2° to 80°. This experimental set-up under a 40KV accelerating voltage and a current of 30mA, and employed nickel-filtered Cu-k_α radiation (λ=1.5412 Å). Coupled θ-2θ scans with a step size of 0.02° and a scan rate of 2°/minute were used.

Thermogravimetric and differential thermal analyses performed on SETARAM a simultaneous TG-DSC thermoanalyzer; model TG-DSC111, with a heating rate of 10degree / min, in static air from 273K to 1223K using a platinum crucible, and flow rate of the controlling gas (air) of 20 ml / min.

The crystal and morphology of the synthesized samples were examined using SEM micrographs were obtained using a LEO SEM 525-20 kV fitted with an EDAX spectrometer, allowing quantitative elemental analysis, and JSM-5400F

SEM with field emission gun and a maximum voltage of 30 kV.

3. RESULTS & DISCUSSION

3.1. Composition of titanium silicate under study

Titanium silicate ETS-10 with Si / Ti ratio of 5.0 possesses one Ti and 5.0 Si atoms per unit cell (u.c.). A cation exchange degree of 70 % corresponds to 0.7 Co/u.c. present in Co^{2+}-exchanged ETS-10. A cation exchanged degree of 76 % corresponds to 0.8 Cu / u.c. present in Cu^{2+}-exchanged ETS-10. In Table 1, the chemical compositions of the ETS-10 (sodium form), Co^{2+}-exchanged and Cu^{2+}-exchanged ETS-10 materials are summarized. The samples Co^{2+}-exchanged and Cu^{2+}-exchanged ETS-10 that calcined at high temperature have the same atomic ratio as the samples at room temperature and are, therefore, not listed in Table 1.

Table (1) Unit cell composition of ETS-10, Co^{2+}-exchanged ETS-10 and Cu^{2+}- exchanged ETS-10

Sample	Unit cell composition
ETS-10	$Na_{1.5}K_{0.5}TiSi_5O_{13}$
Co^{2+}-exchanged ETS-10	$Na_{0.8}Co_{0.7}TiSi_{4.9}O_{13}$
Cu^{2+}-exchanged ETS-10	$Na_{0.5}Cu_{0.8}TiSi_5O_{13}$

The differential thermal analysis curve DTA, figure (1) reveals one smooth endothermic peak for the initial loss in H_2O. The second weight-loss is trimodal on the DTA curve and is due to the difference in energy required to drive off additional H_2O molecules [21].

ETS-10 materials demonstrated thermal stability in their as-synthesized form, as calcination above 1023K resulted in a partial loss of structure followed by a complete loss of crystallinity after 1073K calcinations in air. However, after an amorphous phase at 1023K calcination, the structure appeared to develop into a new crystalline phase at temperatures greater than 1023K. The phase changes are highlighted by the TGA curves. The DTA curve shows positive peaks at above 1073K, indicating an exothermic change at this stage.

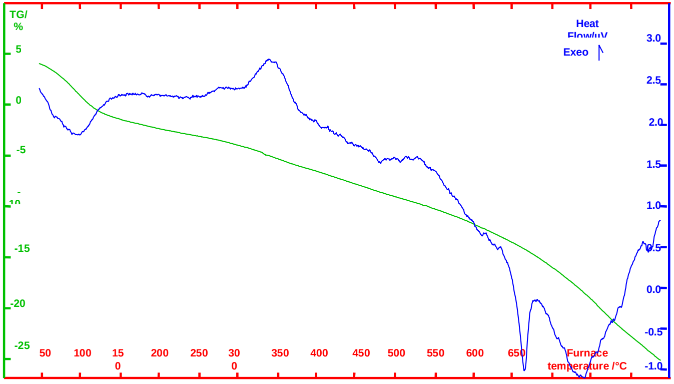

Figure 1:TGA and DTA curves of Titanium silicate ETS-10

3.2. Co^{2+}- exchanged ETS-10:

The Cu-$K_{\alpha 1}$ X-ray powder pattern of Co^{2+}-exchanged ETS-10, shown in figure (2). Upon exchange of titanium silicate, CoNaETS-10, and subsequent calcinations at 523K and 723K, the characteristic reflections of Co^{2+}-exchanged ETS-10 occurring at $5^{\circ} > 2\theta < 80^{\circ}$ are the same as pure ETS-10, and broad background can be observed at around $2\theta = 45^{\circ}$ figure (2b). This background stayed upon calcinations at 1223K figure (2e). The occurrence of the broad background gives evidence for a partial transformation of the framework of Co^{2+}- exchanged ETS-10 material into another phase, and this is supported by the simultaneous changes in the pattern of the characteristic reflections of titanosilicate ETS-10 material. Structural changes occurring as a result of calcinations were analyzed using Panalytical X'Pert High Score program [22]. The legend for identification of the mineral phases is provided in the figure description. The main minerals, which are evident from the X-ray diffraction patterns of calcinated Co^{2+}-exchanged ETS-10 material, are Narsarsukite at 1023K, fig (3a), and formation of a new phase at 1223K is accompanied by a change in the color, this color change is probably associated with the reduction of framework titanium to Ti^{3+} [18].

Figure (3a) illustrates a remarkable resemblance between the powder XRD pattern of the new phase formed after 1023K and that of the synthetic sodium titanium silicate Narsarsukite. All the diffraction lines in the XRD pattern after high temperature calcination have indexed and compared well with JCPDS card for Narsarsukite. Our findings are same from the observations by Anderson et al [18].

The new crystalline phase is thermally stable at 1023K but degrades after several hours of heating at 1223K. The new crystalline phase formed after several hours of heating Co^{2+}-exchanged ETS-10 at 1223K, are shown in figure (3b). All the diffraction lines in the XRD pattern after high temperature calcination have been indexed and compared with JCPDS cards for Rutile, Tridymite, Cobalt oxide and cobalt titanite.

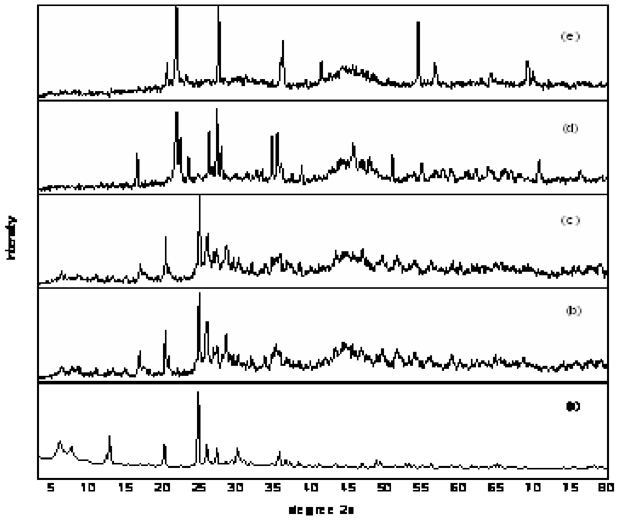

Figure 2 :a) The Cu-$K_{\alpha 1}$ X-ray powder pattern of Co^{2+}-exchanged ETS-10, and subsequent calcinations at (b) 523K , (c)723K, (d)1023K and at 1223K.

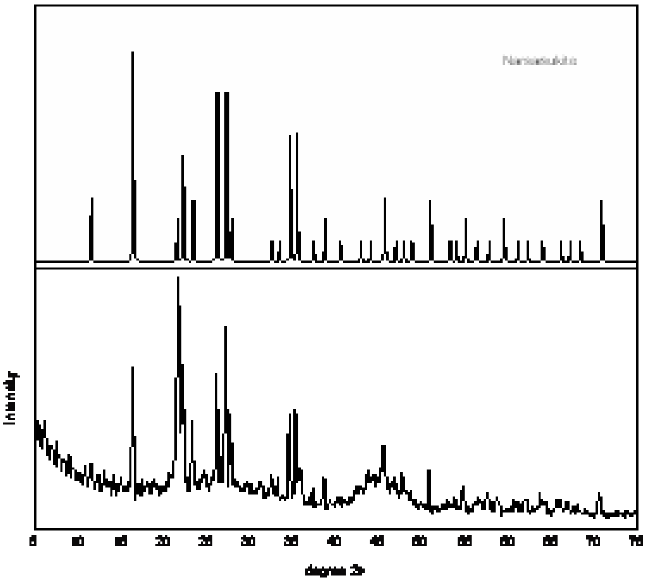

Figure 3: a) powder XRD pattern of the new phase formed after 1023K and that of the synthetic sodium titanium silicate Narsarsukite.

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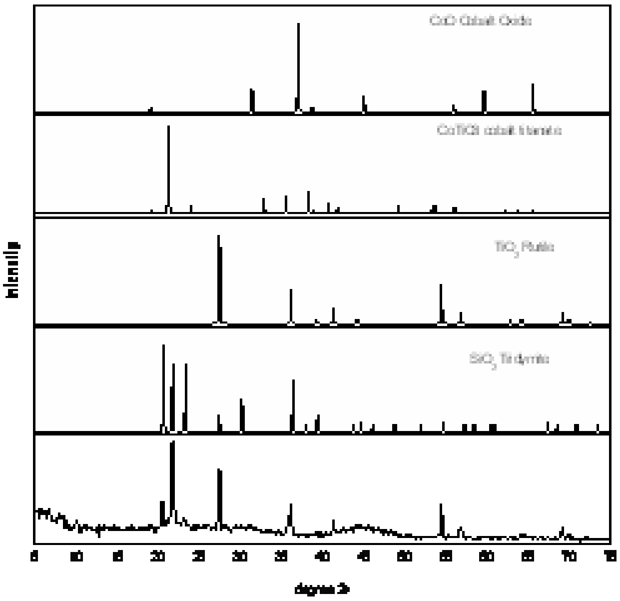
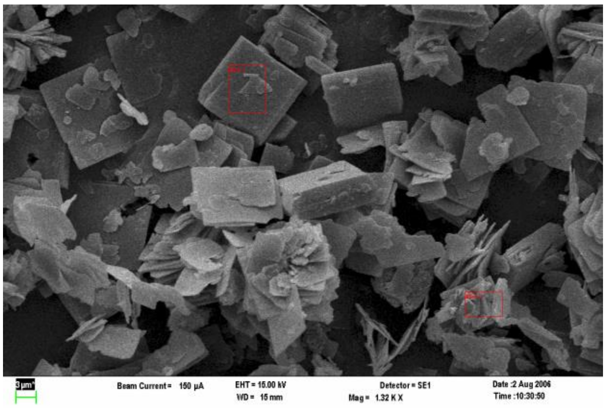
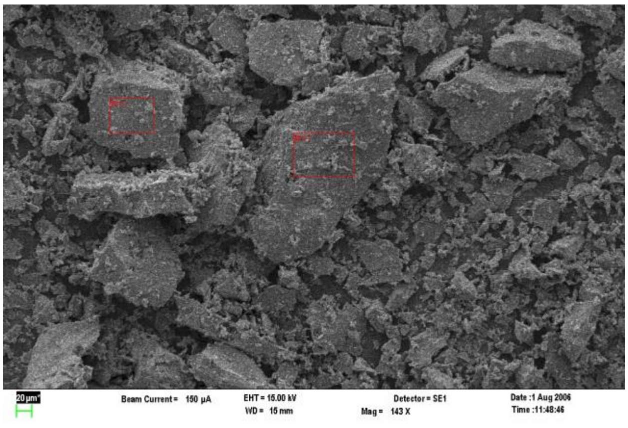


Figure 3:b) XRD pattern after High temperature calcination have been indexed and compared with JCPDS cards for Rutile, Tridymite, Cobalt oxide and cobalt titanite.

Scanning Electron Microscope (SEM) micrograph of the as-synthesized Co^{2+}-exchanged ETS-10 shown in figure (4a). As we can see that when the temperature at 303 K, the products obtained are mainly plate like triangle pyramidal of nanosized particles. After calcinations in presence of air at 1223K SEM micrograph shown in figure (4b), the plate like Co^{2+}-exchanged ETS-10 crystals changes to different irregular shapes.



(a)



(b)

Figure 4: SEM micrograph of the as synthesized Co^{2+}-exchanged ETS-10 (a) and calcined at 1223K (b).

3.3. Cu^{2+}- exchanged ETS-10:

The powder XRD patterns of Cu^{2+}-exchanged ETS-10 after calcination in air from 523K to 1223K are shown in figure (5). The crystal structure of Cu^{2+}-exchanged ETS-10 sample is still intact after heating from 523K to 723K. Most noticeable diffraction pattern of calcinated Cu^{2+}-exchanged ETS-10 at 1023K is the appearance of new reflections which are related to Narsarsukite, Rutile and Tenorite materials as shown in figure (6a). These Findings are different from the observations for Co^{2+}- exchanged ETS-10 material.

The new crystalline phase is thermally stable at 1023K but degrades after several hours of heating at 1223K. These new crystalline phases are shown in figure (6b). All the diffraction peaks in the XRD pattern after high temperature calcination have been indexed and compared with JCPDS cards for Rutile, Copper oxide and Tridymite materials.

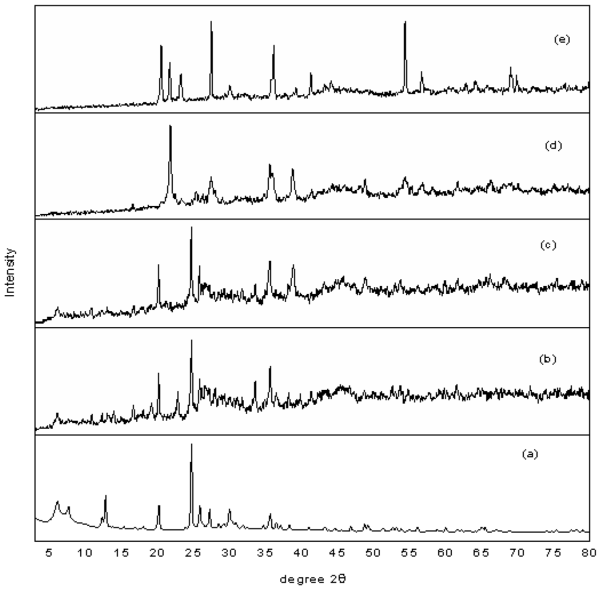


Figure 5: Powder XRD patterns of Cu^{2+}-exchanged ETS-10 after calcination in air from 523K to 1223K.

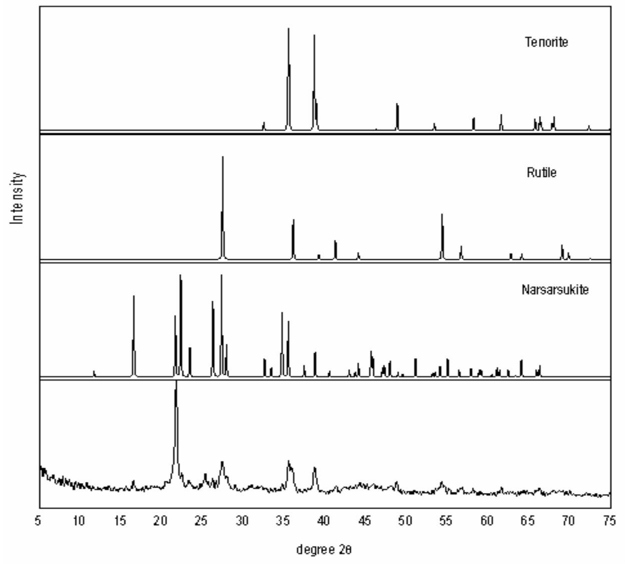


Figure 6: a) diffraction pattern of calcinated Cu^{2+}-exchanged ETS-10 at 1023K is the appearance of new reflections which are related to Narsarsukite, Rutile and Tenorite materials.

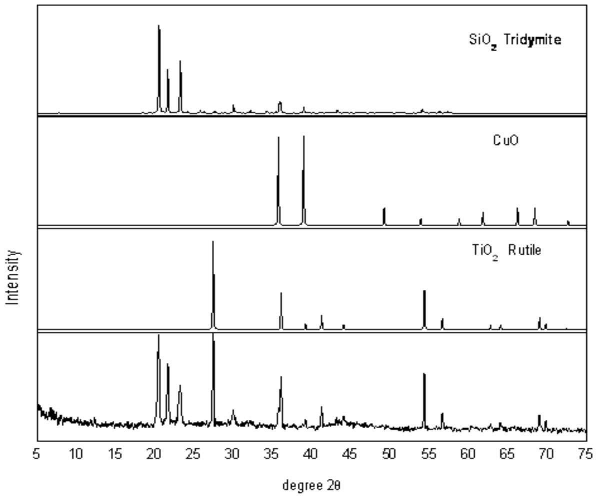


Figure 6: b) Powder XRD pattern of calcinated Cu^{2+}-exchanged ETS-10 at 1023K indexed and compare with JCPDS cards for Rutile, Copper oxide and Tridymite materials.

SEM micrographs of the as-synthesized Cu^{2+}-exchanged ETS-10 at room temperature material is shown in figure (7a), the products obtained are mixture of spherical, long needle and plate like triangle pyramidal shape. Crystal's morphology changes to different irregular shapes on calcinations of Cu^{2+}-exchanged ETS-10 sample in air at 1223K figure (7b).

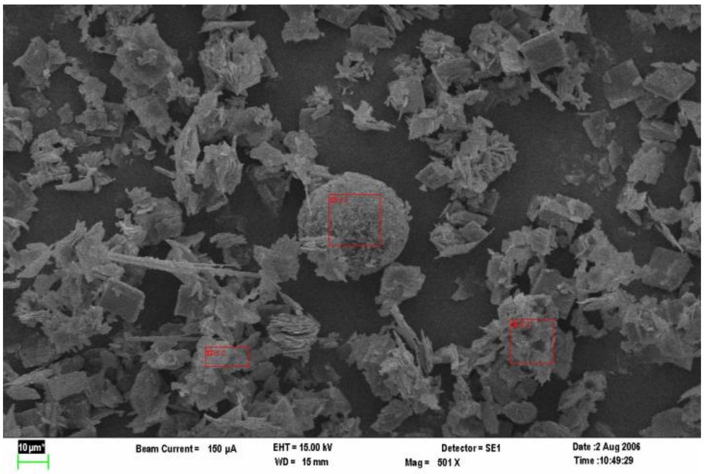


Figure 7a: SEM micrographs of the as-synthesized Cu^{2+}-exchanged ETS-10 at room temperature (a)

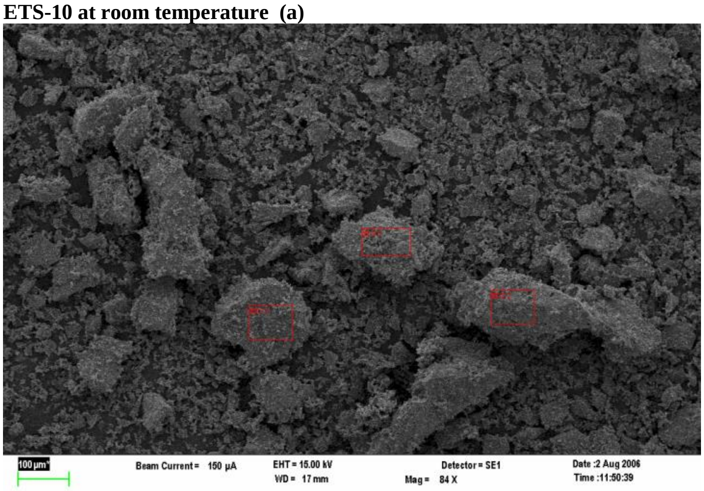


Figure 7b: SEM micrograph of calcinated Cu^{2+}-exchanged ETS-10 sample in air at 1223K (b).

Figure (8) shows The X-ray powder pattern of sodium form of ETS-10 material and its calcinated sample at 1223K. The main mineral, which is evident from X-ray diffraction pattern, is Cristobalite mineral. The results are different to those described above for Cu^{2+}-exchanged ETS-10 and Co^{2+}-exchanged ETS-10 that calcinated at temperatures of 1223K.

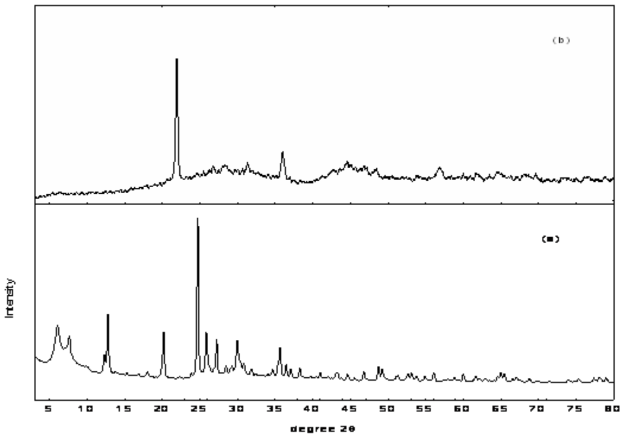


Figure 8:The X-ray powder pattern of sodium form of ETS-10 material (a) and its calcinated sample at 1223K (b).

Figure (2d) shows powder XRD data of Co^{2+}-exchanged ETS-10 material at 1023 K indicate phase transformation of the sample into Narsarsukite. This suggests that the presence of Co^{2+} in the pores makes ETS-10 more prone to thermal decomposition. The powder XRD patterns of Co^{2+}-exchanged ETS-10 calcinated at 1223K figure (2e) indicate that all Narsarsukite materials transformation into Rutile, Tridymite, cobalt oxide and cobalt titanite materials.

The powder XRD pattern of Cu^{2+}-exchanged ETS-10 heated at 1023 K, figure (5d), indicate that the material transformed into Narsarsukite, Rutile and Tenorite. This suggests that the presence of Cu^{2+} in the pores makes ETS-10 more prone to thermal decomposition, where powder XRD patterns of Cu^{2+}-exchanged- ETS-10 calcined at 1223K figure (6b) shows that all materials transformed into Rutile, Copper oxide and Tridymite. However, Naderi et al. [18] has reported that titanium silicate ETS-4 material transformed into Narsarsukite structure in calcinations at 973K.

4. CONCLUSIONS

Despite the apparent intermediate thermal stability of the microporous titanosilicate ETS-10, this material undergoes a series of interesting structural rearrangements upon heating. The material retains a flavor of its original structure up to ca. 723K before further phase transformation. At high temperatures Narsarsukite is formed via an intermediate material. By concentrating effort on the stability of the linking pillar units in ETS-10, the stability of this material could possibly improved.

The method for preparing Exchanged ETS-10 microporous titanosilicates containing Co^{2+} and Cu^{2+}, the metal ions incorporated into the pores of ETS-10 via conventional ion-exchange techniques and the resulting materials calcined in air at a temperature 523 - 723K. The powder XRD and SEM micrographs results show that Cu^{2+}-exchanged ETS-10 and Co^{2+}-exchanged ETS-10 (calcined and non-calcined) essentially retain the structural integrity of the titanosilicates. As the calcination temperature increases, several phase transformations occur, upon heating between 1023K and 1223K.

The phase transformation of titanium silicate ETS-10 in Na-form, Co/Na, and Cu/Na-exchanged form that subjected to high temperature at 1223K is different, where Cristobalite in case of Na-form was formed and Tridymite and metal oxide in case of Co and Cu forms.

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