

SYNTHESIS OF LEUCITE AND KALSILITE FROM ALUMINOSILICATE PRECURSORS

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INTRODUCTION

The sequence of transformation: crystalline phase of potassium exchanged zeolite A \Rightarrow amorphous phase \Rightarrow kalsilite+kaliophilite indicates that the transformation does not occur by a direct way, i.e. by the reorganization (rotation, translation) of primary and secondary building units of zeolite framework into other crystalline phases (kalsilite, kaliophilite or leucite), but that nucleation and crystal growth of the nonzeolitic end product take place by reaction of primary building units (SiO_4 and AlO_4 tetrahedra) of the amorphous phase. Formation of the amorphous phase before their subsequent transformation into kalsilite and kaliophilite leads to an assumption that the activation energy of the breaking of "external" Si-O-Si and Si-O-Al bonds of zeolite is lower than the activation energy of the appropriate rotation and translation of primary and secondary building units of zeolite framework [1]. For this reason, in this study we investigated the direct crystallization of the amorphous K-aluminosilicate gels precursors into non-zeolitic crystalline phases.

EXPERIMENTAL

Me-aluminosilicate hydrogel and the corresponding amorphous Me-aluminosilicate precursor (Me-gel) were prepared by two different procedures: (A) by ion-exchange of sodium ions from zeolitic Na-aluminosilicate gel with the alkaline cation K resulting in K-gel(A) and (B) by direct precipitation from the corresponding K-aluminate and K-silicate solutions resulting in K-gels(B). The chemical composition of the obtained K-gel (A) as is derived by chemical analysis: $0.015\text{Na}_2\text{O} \times 0.985\text{K}_2\text{O} \times \text{Al}_2\text{O}_3 \times 2.576\text{SiO}_2 \times 2.28\text{H}_2\text{O}$. The chemical composition of the obtained K-gel (A) as is derived by chemical analysis: $\text{K}_2\text{O} \times \text{Al}_2\text{O}_3 \times 3.3\text{SiO}_2 \times 2.464\text{H}_2\text{O}$. The K-aluminosilicates prepared by both the mentioned methods as well as the products of their solid-state, high-temperature transformations were analyzed/characterized by different methods such as X-ray diffraction (XRD), X-ray dispersive analysis (EDAX), differential thermal analysis (DTA), differential scanning calorimetry (DSC) and nitrogen absorption (BET).

RESULTS AND DISCUSSION

The temperatures at which possible thermal transformations of the gels take place were found out by differential scanning calorimetry (DSC) of the gels. Figs. 1A and B show that the possible structural changes are indicated by slow corrected heat flows in relatively wide temperature range, 1238 -1313K and 1253-1353 K respectively. In order to heat for less time both the gels were treated at 1523 K for 3h.

The end products characterised by X-ray diffraction is leucite (KAlSi_2O_6 , 01-071-1147) for the gel obtained by procedure A (fig.2A,b) and kalsilite (KAlSiO_4 , 11-0579) for the gel obtained by procedure B (fig.2B,b).

BET measurements of the two gels show a big difference in the specific surface indicating different structural properties. High BET specific surface area of the amorphous

phases K-gel(A) ($53\text{m}^2/\text{g}$) and K-gel(B) ($183,2\text{m}^2/\text{g}$) are the consequence of great internal surfaces of these amorphous phases caused by their (micro/meso)-porous nature. However, due to higher content of water, the gel prepared by procedure B is more porous than the gel prepared by procedure A, and thus the BET specific surface area of the K-gel(B) is considerably higher than the BET specific surface area of the K-gel (A). High temperature transformation of both the gels yield to a dense ceramic material with relatively low BET surface.

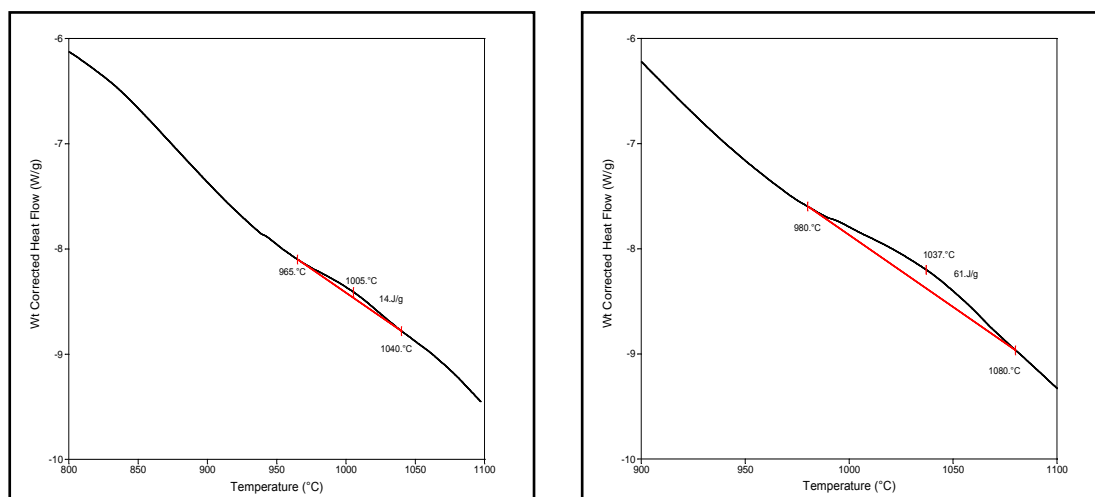


Figure 1. DSC curves of the amorphous K-aluminosilicate precursors obtained by Procedure A (a) and by Procedure B (b).

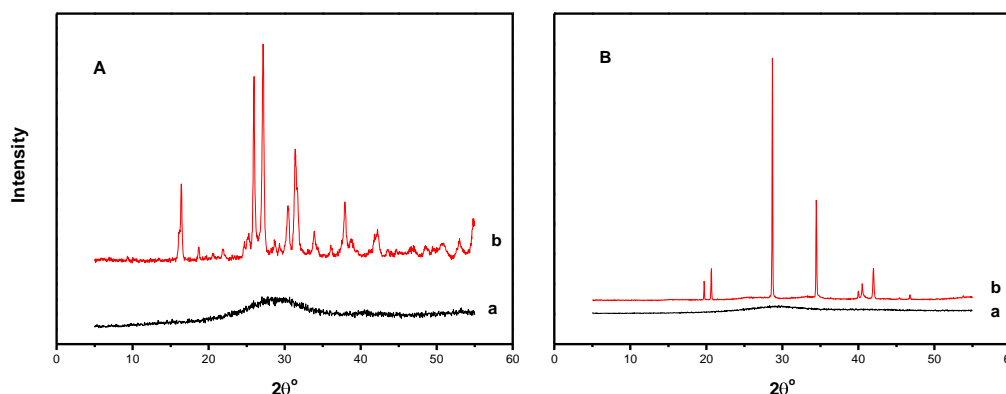


Figure 2. X-ray diffraction(XRD) patterns of the samples obtained before (a) and after (b) the thermally induced transformations of the amorphous K-aluminosilicate precursors obtained by Procedure A (A) and Procedure B (B).

Table 1. BET surface area of amorphous and crystalline phases, temperature and time of thermal treatment of the samples

Sample	Amorphous phase BET(m^2g^{-1})	Temperature ($^{\circ}\text{C}$)	Time (h)	Crystalline phase BET (m^2g^{-1})
K-gel (A)	53	1250	3	0.2
K-gel (B)	183.2	1250	3	0.2

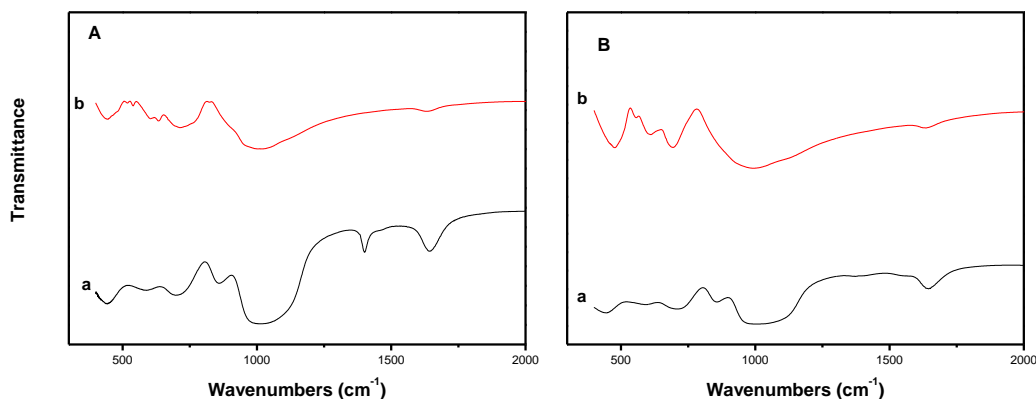


Figure 3. FT-IR spectra of the samples obtained before (a) and after (b) the thermally induced transformations of the amorphous K-aluminosilicate precursors obtained by Procedure A (A) and Procedure B (B).

The differences in structural properties of the amorphous phases that are also evident in FT-IR spectra (see fig.3A a and 3B a) cause the pathway of transformation to pure leucite or kalsilite respectively.

CONCLUSIONS

Although the crystallization of kalsilite/kaliophilite was expected during the heating of both K-gel (A) and K-gel(B) [1,3], only kalsilite (KAlSiO_4 , 11-0579) [4] was crystallized during the heating of K-gel(B) the heating of K-gel(A) resulted in the crystallization of leucite (KAlSi_2O_6 , 01-071-1147). It is obvious that the "gel structure" consists of different primary and secondary structure units that influence the formation of a certain crystallization product.

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SINTEZA LEUCITA I KALSILITA IZ ALUMOSILIKATNOG PREKURSORA

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SAŽETAK

Izotermalna kristalizacija rendgenski amorfnih K–alumosilikata ($x_1\text{Na}_2\text{O}$, $x_2\text{K}_2\text{O}$) \times $\text{Al}_2\text{O}_3 \times y\text{SiO}_2 \times z\text{H}_2\text{O}$) (pripremljenih na 2 načina: (A) ioskom izmjenom iona natrija iz zeolitnog Na–alumosilikata sa alkalnim kationom K koja rezultira nastajanjem K-gela (A) i (B) izravnim taloženjem iz pripadajuće K-aluminatne i K-silikatne otopine koje rezultira nastajanjem K-gela (B)) na utvrđenim temperaturnim rasponima ispitane su metodom rendgenske difrakcije.

Analize faza transformacijsko-kristalizacijskih procesa pokazale su da: čisti kristalni tetragonski leucit kristalizira iz K-gela (A) u temperaturnom rasponu grijanja od 1238 K do 1313 K dok čisti heksagonalni kalsilit kristalizira iz K-gela (B) u temperaturnom rasponu grijanja između 1253 i 1353 K.

K-alumosilikati pripremljeni prema navedenim metodama i produkti njihovih visokotemperaturnih transformacija analizirani su/karakterizirani različitim metodama, kao što je rendgenska difrakcija (XRD), disperzivna rendgenska analiza (EDAX), diferencijalna termička analiza (DTA), diferencijalna pretražna kalorimetrija (DSC) i apsorpcija dušika (BET). Kemijska analiza gelova pokazuje da razmjena prvotnih natrijevih iona iz gela pripremljenog po postupku (A) [Na-gel(A)] ne mijenja značajno kemijski sastav, strukturna (XRD i DTG profili) i fizička svojstva (specifična površina). Termička obrada svih gelova rezultirala je njihovom pretvorbom u odgovarajuće faze kristalnog alumosilikata čiji je sastav KAlSiO_4 , odnosno KAlSi_2O_6 . Sve pretvorbe prati drastično smanjenje specifične površine BET uzrokovane prijelazom (mikro/mezo)-poroznih amorfnih Me-aluminosilikata u gušće, neporozne kristalne faze.

Ključne riječi: amorfni alumosilikati, termička pretvorba, keramika