

PREPARATION OF ZEOLITE X COATINGS ON SODA-LIME TYPE GLASS PLATES

M. Tatlier* and Ç. Atalay-Oral

Department of Chemical Engineering, Istanbul Technical University, Maslak, 34469 Istanbul, Turkey.
Phone: + 902122856234; Fax: + 902122852925
E-mail: tatlierm@itu.edu.tr

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Abstract - The dissolution of glass in highly alkaline reaction mixtures and the impact of this phenomenon on zeolite coating formation were investigated. Coating samples were prepared and characterized by X-ray diffraction (XRD), field emission gun scanning electron microscopy (FEGSEM) and thermogravimetry (TG). It was demonstrated that zeolite X coatings might be prepared on soda-lime glass. Glass dissolved to some degree, up to 2% of its original mass, in the reaction mixtures for the conditions investigated. This dissolution affected the zeolite synthesis taking place on the glass surface, resulting in phases different from those obtained on inert metal surfaces in some cases, especially for the use of reaction mixtures with relatively high Si/Al ratios. The percentage of dissolution of glass plates increased with their decreasing thickness, indicating a surface phenomenon for the dissolution. The stabilities of the coatings, which varied with the synthesis conditions, benefited from the addition of extra thin layers of polyacrylic acid.

Keywords: Glass; Zeolite; Coating; Crystallization; Composite.

INTRODUCTION

Zeolites are hydrated aluminosilicates that have many useful existing and potential applications related to adsorption/separation, catalysis and ion-exchange. Utilization of zeolites in the form of coatings may provide advantages such as faster heating cooling, lower pressure drop and easier manipulation of the adsorbent layer thickness. Zeolites have been directly crystallized on different substrates by using different techniques, the simplest of which involves the immersion of the substrate in the reaction mixture heated by a water bath/oven. This conventional synthesis method is often insufficient to provide coatings with the desired properties for different zeolites and applications. Growing thick coatings may be difficult for very metastable zeolite phases which convert rather quickly into other phases during synthesis. One of the extreme cases is zeolite A, for which coating thicknesses higher than 5 μm

can hardly be achieved in one conventional synthesis step. This difficulty may be overcome by using the substrate heating method where the substrate is heated directly while the reaction mixture is kept at a lower temperature (Erdem-Senatarlar *et al.*, 1999). This method may allow a better manipulation of zeolite synthesis by controlling the temperature of the metal substrate and the temperature of the bulk reaction mixture separately. Growing relatively thin and homogeneous coatings may also be difficult due to the delicate competition between nucleation and crystal growth. The seed film method may be useful in this respect (Valtchev *et al.*, 1996). This technique involves the pre-treatment of the substrate, aiming for a surface charge reversal followed by the electrostatic adsorption of colloidal crystals of molecular sieves onto the substrate surface and finally the growth of crystals into a dense and continuous film of inter-grown crystals by treatment in an appropriate synthesis solution under hydrothermal conditions.

*To whom correspondence should be addressed

Some other techniques, such as dip coating and pulsed laser deposition may also be used for preparing zeolite coatings on substrates. These methods are not involved with direct crystallization of the zeolite on the support material. Dip coating generally requires a binder, but may allow an easier control over the coating preparation process (Zhang *et al.*, 2012). In the pulsed laser deposition method, coatings of zeolites may be prepared on the support by the laser ablation of the as-synthesized zeolite pellets (Deng and Balkus, 2002).

Up to now, zeolite coatings have been grown on different types of substrates. Owing to the remarkably stable nature of stainless steel, even in highly alkaline and corrosive environments, this metal has been commonly used (Bonaccorsi and Proverbio, 2004; Fankhanel *et al.*, 2009). Copper becomes less stable in the presence of high alkalinity, but this does not preclude the formation of thick coatings (Teber *et al.*, 2010). The preparation of zeolite on aluminum involves the use of this metal as both the support and reactant in the reaction mixture (Calabrese *et al.*, 2014). Other supports, such as silicon wafers (Dong *et al.*, 2005) and various ceramics, have also been coated by zeolites. Films of zeolite were grown on the walls of ceramic cordierite supports using a seeding technique (Mosca *et al.*, 2010), while ceramic foams were coated with zeolite crystals by *in-situ* crystallization from a precursor sol (Snijkers *et al.*, 2005). The growth of zeolite layers by *in situ* crystallization on zircon porous supports (Falamaki *et al.*, 2006) and α -silicon carbide supports (Losch *et al.*, 2014) has also been investigated. Zeolite membranes have been commonly prepared on ceramic surfaces, such as macroporous alumina (Sheng *et al.*, 2011) and nanoporous alumina supports (Jia *et al.*, 1994). Coatings of zeolites on glass may also be favorable for some applications, such as dehumidification, deodorization and provision of heating/cooling, since glass objects are used very commonly in daily life. However, there are not so many studies in the literature on this issue, probably since glass may dissolve readily in the rather alkali zeolite synthesis mixtures, especially in those that are used to prepare zeolites with relatively low Si contents, such as zeolites A and X. It is not straightforward to prepare zeolite coatings on glass due to this dissolution. The few related studies include the use of a soft-solution process for *in situ* coating of faujasite type (zeolite X/Y) crystals on commercial $\text{SiO}_2\text{-Al}_2\text{O}_3$ glass fibers from NaOH solutions containing NaCl as a mineralizer (Okada *et al.*, 2000). Another study investigated the *in-situ* coating of zeolite NaA crystals on $\text{SiO}_2\text{-Al}_2\text{O}_3$ glass fibers by treating the fibers with various

concentrations of NaOH solutions (Okada *et al.*, 1998). Crystals of zeolite NaA was observed to precipitate on the glass fibers when the concentrations of Si and Al components in the solution increased by dissolution of the glass fibers. Some efforts have also been made to coat glass by relatively high-Si zeolites, such as ZSM-5/silicalite and BEA, which use relatively less alkaline reaction mixtures. Some of these involve the modification of the glass surface, the use of neutral reaction mixtures or indirect coating methods, such as dip-coating to prevent the dissolution of glass during synthesis. ZSM-5 could be deposited on glass fibrous supports (Louis *et al.*, 2001). Here, a homogeneous coverage of the support filaments was obtained by the synthesis of zeolite crystals in fluoride-containing media at neutral pH of about 7. Zeolite Beta films with 1–2 μm thickness were synthesized on borosilicate glass, previously coated by two thin films of zirconia and titania by atomic layer deposition, which protected the glass substrate from dissolution in the highly alkaline synthesis mixture (Muraza *et al.*, 2008). Highly *b*-oriented silicalite-1 thin films were obtained by hydrothermal synthesis on glass slides modified with Ti–OH groups by a surface sol–gel process (Di *et al.*, 2011). The modification of the glass substrate by the TiO_2 layers greatly increased the density and reactivity of the surface hydroxyl groups. Scratch resistant anti reflection BEA coatings were prepared on glass by the dip coating of a mixture containing aggregated zeolite nanoparticles as the structure provider and zeolite precursors as the reactive binder (Chen *et al.*, 2011). ZSM-5 crystals were coated on mesoporous glass materials with hierarchical trimodal pore size distributions by hydrothermal synthesis to introduce microporosity (Louis *et al.*, 2010).

In spite of some studies performed on zeolite coating formation on glass, these generally have not utilized conventional highly alkaline zeolite synthesis mixtures and/or conventional procedures. Not much information is available about the effect of glass dissolution on zeolite synthesis, either. However, zeolite synthesis occurring along with glass dissolution may also be significant, e.g., it may allow the production of composite materials for different applications. In this study, coatings of zeolite X were targeted to be formed on ordinary soda-lime type glass plates from three different highly alkaline synthesis mixtures conventionally known to produce zeolite X. Hydrothermal synthesis was carried out and the samples were characterized by X-ray diffraction (XRD), field emission gun scanning electron microscopy (FEGSEM) and thermogravimetry (TG).

The mechanical stabilities of the coatings were determined. The dissolution of glass plates in alkaline mixtures was also investigated by separate experiments.

EXPERIMENTAL

Hydrothermal synthesis was performed in an oven kept at 80 °C for 6-42 h. Clear reaction mixtures with molar compositions of 70 Na₂O:Al₂O₃:26 SiO₂:2100 H₂O (C1), 70 Na₂O:Al₂O₃:18 SiO₂:2100 H₂O (C2) and 70 Na₂O:Al₂O₃:15 SiO₂:2100 H₂O (C3), in the composition range previously shown to yield zeolite X on stainless steel (Tatlier *et al.*, 2008), were selected. The glass plates had a 5x5 cm² surface area and were about 3.5 mm in thickness. They were immersed in reaction mixtures of about 150 ml, which were placed in polypropylene reactors. The glass plates had a molar composition (%) of about 69.7SiO₂: 20.6Na₂O: 4.4CaO: 3.2MgO: 0.16Al₂O₃: 1.8C: 0.14SO₃. The solubilities of the plates in the highly alkaline reaction mixtures were determined separately by using two different compositions of 70 Na₂O:15 SiO₂:2100 H₂O (C4) and 47.4 Na₂O:15 SiO₂:2100 H₂O (C5) that did not contain alumina so that zeolite formation would not appreciably occur in the system. The alkalinity of C4 was similar to those of C1-C3 (pH of about 12.8) while C5 was less alkaline. Additional glass plates with different thicknesses of about 2 mm, 3.5 mm and 6 mm (surface area=1x1 cm²) were investigated to determine the effect of surface area/volume ratio, or plate thickness, on the percentage dissolution of glass in the mixtures.

The coatings prepared were characterized by XRD (Pananalytical X'Pert Pro), TG (Shimadzu TA-503) and FEGSEM (JEOL JSM-7000F). XRD and FEGSEM were applied for phase identification and morphological investigation of the samples, respectively, while TG analysis was performed to determine water desorption between ambient temperature and 350 °C under nitrogen flow. A heating rate of 20 °C/min was used and different samples prepared under the same synthesis conditions were tested in order to assure that similar results were obtained. Prior to the TG measurements, the samples were kept in a desiccator under a controlled humidity atmosphere (saturated NH₄Cl solution) and were saturated until their mass remained constant. The glass plates used in this analysis had a surface area of 1x1 cm² and thickness of 2 mm. The mass of the zeolite coatings varied between 6-8 mg, which were obtained after 18-42 h of synthesis.

Some of the zeolite coatings prepared were covered with thin polymer films. This was shown previ-

ously to improve the stabilities of zeolite on stainless steel substrates (Atakan *et al.*, 2012). For this purpose, a solution containing 4% (by weight) of polymer was prepared from commercial polyacrylic acid (Aldrich, MW=450000 g/mol). The glass substrates coated with zeolite were immersed for a short time in the polymer solution placed in a small container and then the composite materials obtained were dried overnight at room temperature. The mechanical stabilities of the zeolite and composite coatings were investigated by their treatment in an ultrasonic bath (Sonorex, 35 kHz) for 30 min at a temperature of 30 °C. Accordingly, the materials were placed in polypropylene containers filled with acetone, which was selected as the medium for the transmission of ultrasonic waves since polyacrylic acid may be soluble in water. The samples were kept in a desiccator under a controlled humidity atmosphere (saturated NH₄Cl solution) and weighed at the beginning and end of the stability tests in order to determine the loss of film mass.

RESULTS AND DISCUSSION

The mass of soda-lime type glass plates decreased with time when they were kept in the solutions C4 and C5 at 80 °C. The variation of the amount of dissolution (in %) with respect to time may be seen in Figure 1 for plates of different thicknesses, which all had about a 1x1 cm² surface area. The mass loss approached 2% of the original glass mass after 47 h in the more alkaline solution C4 when the thinnest plate (2 mm) was utilized. The percentage mass loss decreased for the thicker plates which had lower surface area/volume ratios. Thus, it may be speculated that dissolution of the glass occurred preferentially from the plate surface. The dissolution of glass might provide some reactants used in zeolite synthesis. The most prominent one is silica. It was estimated that the contribution of silica from the glass would change the compositions of the reaction mixtures C1-C3 only by about 1.0-1.5%, even in the most extreme cases in this study. The possible changes induced by Na₂O and Al₂O₃ in the compositions of the reaction mixtures should be much less.

Figure 2 shows the variation of the amount of glass dissolved (in %) with respect to the thickness ratio, which may be defined as (6 mm/thickness of any glass plate). In other words, the thickness ratio of the 6 mm sample was taken to be equal to 1 while those of 3.5 mm and 2 mm samples became equal to 1.714 and 3, respectively. Two treatment durations of 30 h and 47 h in the alkaline mixture C4 were taken

into consideration. A rough prediction was also made by assuming that the linear relationship obtained for the three samples investigated in this study also held true for lower glass plate thicknesses. Accordingly, it was estimated that, for the treatment duration of 30 h, 20% and 50% dissolution of glass may be achieved when glass plates with thicknesses of 134 μm and 54 μm are used, respectively. When the longer treatment time of 47 hour is taken into account, 20% and 50% dissolution of glass may be achieved for plate thicknesses of about 176 μm and 70 μm , respectively. In other words, increases made in the surface area/volume ratio of the glass plates by decreasing their thickness allow for relatively high percentage dissolution of glass in alkaline zeolite synthesis mixtures. This may indicate that zeolite-glass composite materials, such as membranes, could be obtained when the openings in thin sheets of dissolving glass are covered by zeolite.

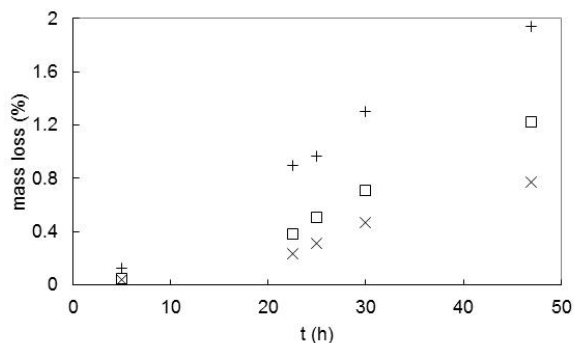


Figure 1: Variation of the mass of glass dissolved with respect to time in solutions with compositions (\square) C4 (for 3.5 mm thick glass), (+) C4 (for 2 mm thick glass) and (x) C5 (for 3.5 mm thick glass).

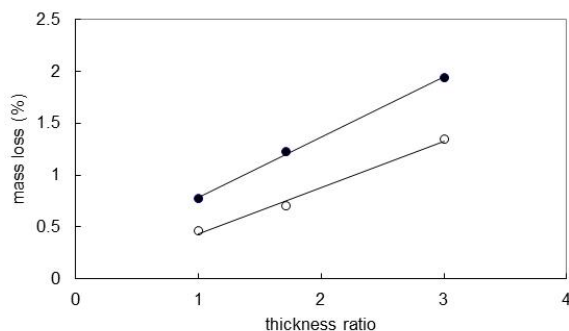
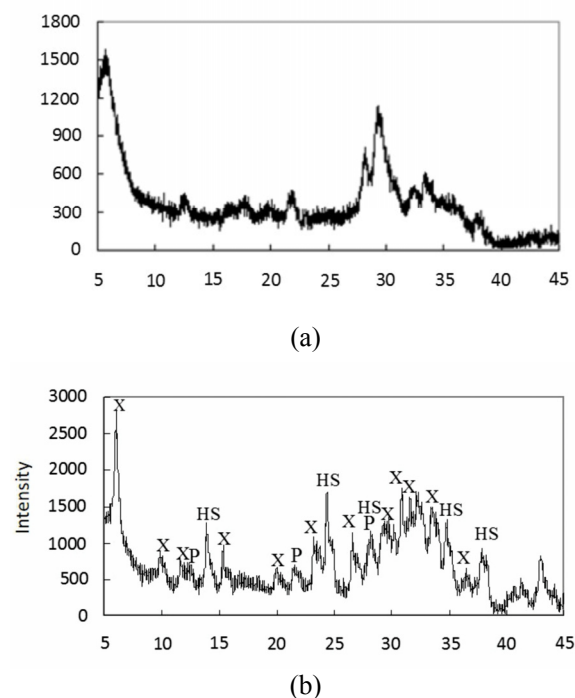


Figure 2: Variation of the amount of glass dissolved with respect to the thickness ratio defined as (6 mm/thickness of any glass plate) for (o) 30 h and (●) 47 h of treatment in the mixture C4.

According to XRD analysis, 6-42 h of synthesis employing compositions C1 and C2 did not allow the

preparation of pure and crystalline zeolite X on glass. Actually, no observable coating was formed after 6 h of synthesis. The XRD pattern of the sample prepared from C1 after 24 h of synthesis is shown in Figure 3(a). The presence of amorphous material with some zeolite P may be mainly observed from the pattern. This contradicts the result (zeolite X) obtained previously on stainless steel plates under the same synthesis conditions (Tatlier *et al.*, 2008). Thermogravimetric analyses were also performed for the samples prepared from composition C1 and it was observed that the desorption capacities obtained after the initial TG measurements (≈ 0.20 - 0.24 g/g hydrated coating) decreased to about 0.05-0.06 g/g hydrated coating in the second run for all the samples prepared after 18-42 h of synthesis. This confirmed the highly amorphous nature of the coatings. On the other hand, the desorption capacity of the zeolite X coating grown on stainless steel (316 L) from composition C1 after 24 h decreased from 0.22 g/g hydrated zeolite to only 0.21 g/g hydrated zeolite in the second run, indicating quite high crystallinity. The XRD pattern of the sample prepared from composition C2 after 24 h of synthesis is shown in Figure 3(b). In this case, when the Si/Al ratio of the reaction mixture was decreased, zeolite X formation was favored but the coating was a mixture of zeolites X, P and hydroxysodalite (HS), while some amorphous material also seemed to exist, again contradicting the result (zeolite X) obtained using stainless steel as the substrate.



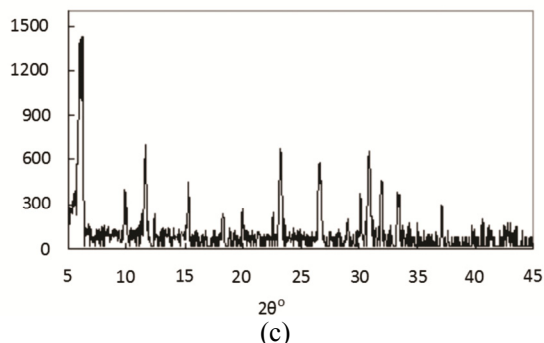


Figure 3: XRD patterns of the coatings prepared on glass after 24 h of synthesis from compositions (a) C1, (b) C2 and (c) C3.

As the Si/Al ratio of the reaction mixture was decreased further, pure zeolite X could be crystallized on soda-lime type glass plates from composition C3 after different periods of synthesis (18 h, 24 h and 32 h), as confirmed by XRD and TG measurements. This result was similar to that obtained employing the same composition on stainless steel substrates (Tatlier *et al.*, 2008). The XRD pattern of the sample prepared after 24 h of synthesis is shown in Figure 3(c). The TG curves of the coatings, including the one grown on stainless steel, may be seen in Figure 4 for synthesis times of 18-42 h. The desorption capacities varied between 0.21-0.24 g/g hydrated zeolite in the temperature range investigated. The somewhat different curve obtained for the synthesis time of 18 h might be related to a slightly lower crystallinity for this sample. A lower desorption capacity was obtained for the sample prepared after 42 h of synthesis, which indicated the start of transformation of zeolite X to zeolite P, as also confirmed by XRD. The TG curve and desorption capacity of the coating prepared on stainless steel after 24 h were not much different from those of the coating prepared on glass after the same synthesis time. The second TG measurements did not lead to noteworthy reductions in the capacities of all the samples prepared on glass and metal. The desorption capacities were equal to about 0.20-0.23 g/g hydrated zeolite in this case.

FEGSEM photographs of the coating grown on glass (1x1 cm²) from composition C3 after 24 h of synthesis are given in Figure 5 at three different magnifications. The crystals revealed the typical octahedral shape of zeolite X. The coating, comprising crystals of a few microns in size, seemed to be quite homogeneous. The mass equivalent thickness of the mentioned coating, as estimated from the hydrated coating mass/hydrated density of zeolite, was equal to about 17 μm. Local increases of the reactants, especially that of Si, near the dissolving glass surface

may be hypothesized to be responsible for the differences in the results obtained for coatings formed on glass and stainless steel from the same reaction mixture composition, since the bulk composition of the mixture remained nearly the same after the dissolution of glass. Soda-lime type glass is amorphous in nature and mainly consists of tetrahedral units of silicon bonded to four oxygen atoms. These tetrahedral units coming from glass, which are also present in zeolites, or bare Si and other atoms detached from the glass, might have priority compared to reactants present in the reaction mixture in contributing to the formation of crystalline zeolite or an amorphous coating on the glass surface.

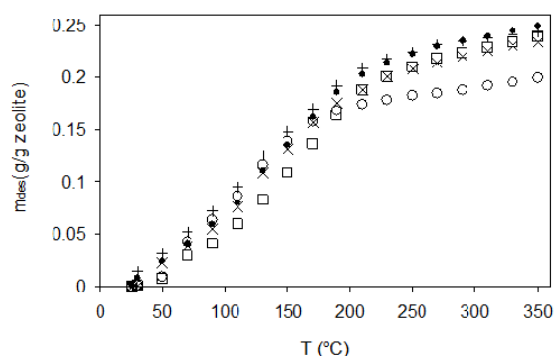
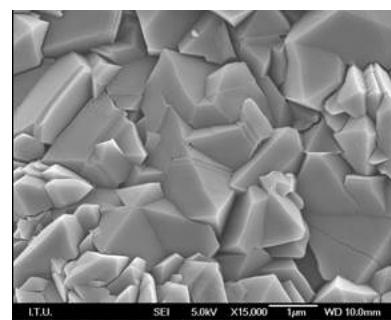
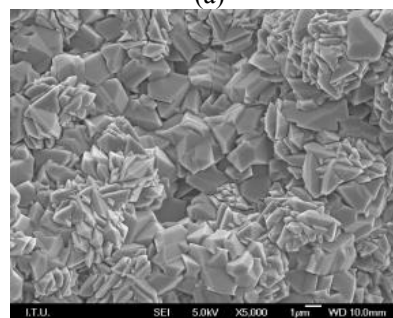


Figure 4: TG curves of the coatings prepared from composition C3 on glass after (□) 18 h, (●) 24 h, (+) 32 h and (o) 42 h of synthesis and on stainless steel after (x) 24 h of synthesis.



(a)



(b)

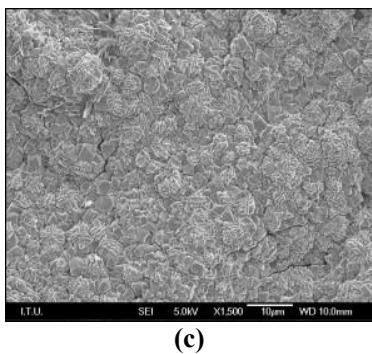


Figure 5: FEGSEM photographs of the coating grown on glass from composition C3 after 24 h of synthesis at magnifications of (a) x15000, (b) x5000 and (c) x1500.

The mechanical stabilities of the coatings prepared with or without the post-synthesis treatment involving their coverage by thin extra layers of polyacrylic acid are reported in Table 1. The mass equivalent thicknesses of the coatings were equal to about 15-20 μm . The mass losses of the glass plates due to their dissolution in the reaction mixtures were taken into account in determining the masses of the zeolite coatings. It was observed that about 61-76% of the zeolite X coatings prepared from composition C3 remained intact after stability tests in an ultrasonic bath, in the absence of the post-synthesis treatment. Stability decreased somewhat after 24 h of synthesis as the coating thickness increased, but after 32 h stability increased again. Stability might be affected by the different stages of synthesis activities, involving the nucleation and crystal growth of zeolite particles, as well as the dissolution of glass during these activities. It is possible that the dissolution of glass, interfering with zeolite synthesis as mentioned before, may also affect the stabilities of the zeolite coatings in different amounts at different stages of synthesis. Covering the zeolite with thin polyacrylic acid layers after synthesis was observed to favor stability to a great extent, similar to the coatings prepared on stainless steel (Atakan *et al.*, 2012). By using this post-synthesis treatment, the mass loss in the coating was almost avoided, reducing it to about 2-3% of the original sample mass.

It was previously observed that the additional thin polyacrylic acid layers covering zeolite coatings did not lead to any reduction in the adsorption/desorption capacities of the samples (Atakan *et al.*, 2012). On the other hand, slightly adverse impacts were observed on the adsorption kinetics, especially after relatively high normalized loadings for the zeolite-polymer composite samples (Atakan *et al.*, 2013). These polyacrylic acid layers were prepared using a

solution containing 4% (by weight) of polymer. The thickness of the polymer coating covering the zeolite may be reduced further for improved kinetics. Overall, there seems to be no significant restriction for the use of zeolite-polymer composites in different applications, such as those related to adsorption and catalysis. Thin zeolite-polymer composites prepared on porous supports could also be tested to see if they have superior separation properties compared to other types of membranes in different processes. Surely, the covering of zeolite coatings by additional polymer layers will be especially useful for increasing their stabilities. It is known that low thermal and mechanical stabilities of zeolite coatings may present serious problems, leading to reductions in the performance of these materials in different applications, such as adsorption heat pumps.

Table 1: Masses and stabilities of coatings prepared by using composition C3 after various synthesis times.

Synthesis time (h)	Post-synthesis treatment	Total mass (mg/25 cm ²)	Mass loss (%)
18	No	149	24
18	Yes	165	2.2
24	No	170	39
24	Yes	189	3.2
32	No	193	25
32	Yes	217	2.6

CONCLUSIONS

It was shown that zeolite X coatings could be prepared on soda-lime type glass plates. Some dissolution took place for glass in the quite alkaline reaction mixtures, although this did not change the composition of the reaction mixture significantly. All the same, two of the reaction mixture compositions tested led to the formation of different materials on glass and stainless steel substrates under the same synthesis conditions. This signifies the interference of glass with zeolite formation, which may be speculated to be related to the presence of a higher concentration of Si near the glass surface than in the bulk of the synthesis mixture. Such a phenomenon might result in zeolite phase shifts under certain conditions, as in the two examples of relatively high-Si content reaction mixtures used in this study.

Actually, the direct crystallization of low-silica zeolites, such as zeolite X on glass is not a very predictable process due to the dissolution of glass in the highly alkaline reaction mixtures that have to be used for these syntheses. This study should contribute to a

better understanding and manipulation of zeolite synthesis on soda-lime type glass commonly used in daily life. It should also be remembered that, although the dissolution of glass seems to complicate the zeolite synthesis process, it may also open the route to the preparation of useful composite materials, such as those that may be obtained in the case when a relatively high ratio of dissolved mass to original glass mass is achieved. In this study, it was estimated that glass with 20-50% porosity should be obtained when plates (sheets) with thicknesses of about 50-150 μm are treated in alkaline reaction mixtures under the conditions investigated. The openings in glass may be filled/covered by zeolite crystallized from the reaction mixtures. This may provide us with special composite materials, such as zeolite-glass membranes for separation processes. Some detachment of about 24-39% of the original coating mass took place during the stability tests, but this situation could be almost totally avoided when the zeolite coatings were covered by additional thin layers of polyacrylic acid. Different synthesis conditions and methods may be tested to vary the coating thickness as well as to improve the coating stability further when application of the mentioned post-synthesis treatment is not preferred.

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