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Positron Annihilation Lifetime Spectroscopy Study of the Formation of Mesoporous Materials from the Zeolite Precursor

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In this work, positron annihilation lifetime spectroscopy was used for the structural characterisation of porous materials prepared from amorphous zeolite precursors acting as the starting materials and hexadecyltrimethylammonium bromide acting as a mesoporous template. The best fits of the obtained lifetime spectra provide a four-component exponential decomposition. The lifetime values of the long-lived components point to the presence of mesoporous voids. Infrared and X-ray analyses show that the obtained materials consist partly of a crystalline zeolite structure.

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1. Introduction

Zeolites are specific crystalline microporous materials used in adsorption, catalysis, ion-exchange, molecular sieving etc. [1]. Still, in some applications, for example in catalysis, microporous channels can be a restricting factor, as the diffusion of bulkier molecules within the structure is limited which reduces the functionality of the zeolite material [2]. Therefore, introducing mesoporosity into the microporous zeolite structure, or producing materials with both micro- and mesoporosity could, at the same time, retain zeolite properties and help to remove limitations [3].

Positron annihilation lifetime spectroscopy (PALS) has become a well-proven technique in the structural characterisation of zeolites [4–6]. The study covered changes of the void sizes influenced by the presence of non-framework cations [7], water molecules [8–10], phase transitions [11] or cluster formations [12]. PALS was also successfully used in investigating mesoporous voids present in silica gel structures [13–15], in ordered mesoporous silica materials [16, 17], and in investigating the presence and removal of a mesoporous template from the structure [18–20].

In this work, PALS was used for the characterisation of porous materials obtained from amorphous zeolite precursors and hexadecyltrimethylammonium bromide acting as a mesoporous template.

2. Experimental

The chemicals used for the syntheses were: fumed silica (SiO₂, Sigma-Aldrich), sodium hydroxide (NaOH 98%, Kemika), sodium aluminate (NaAlO₂, Riedel de Haen), tetrapropylammonium bromide (TPABr 98%,

Sigma Aldrich) and hexadecyltrimethylammonium bromide (CTAB 98%, Alfa Aesar). The amorphous zeolite precursor (original gel) with the molar composition 12.5Na₂O·Al₂O₃·60SiO₂·8TPABr·4000H₂O was prepared according to Ref. [21]. Modifications of the original gel included the following steps: (1) ageing of the original gel for 720 h at room temperature (RT) (modification-1), and (2) preparing the same original gel but without TPABr (modification-2). The mesoporous template, CTAB, was then added to the prepared precursors (molar ratio CTAB/SiO₂ = 6). The syntheses were performed at 80 °C for 72 h and subsequently at 120 °C for 48 h in static conditions. The synthesized samples were calcined in air at 550 °C for 5 h.

The PALS measurements were conducted with a modified version of a digitized positron annihilation lifetime spectrometer [22]. In the present setup, the conical BaF₂ scintillators (bases of 2.5 cm and 5 cm, and height of 2.5 cm) coupled to the XP2020 URQ photomultiplier tubes were used along with the same signal processing and data acquisition chain as in [22]. The time window in the measurements was 100 ns, with the source activity approximately 1 MBq and achieved time resolution about 220 ps. For the each sample, approximately 10⁶ annihilations were recorded. The infrared transmission (FTIR) spectra of the samples were made using the KBr wafer technique. The spectra were recorded in the mid IR region (4000–400 cm⁻¹) on the Spectrometer System 2000 FTIR (Perkin–Elmer). The powder X-ray diffraction (XRD) spectra of the samples were taken using a Philips PW 1820 diffractometer equipped with a vertical goniometer, and using Cu K_α radiation in the corresponding region of Bragg's angles (2θ = 4–100°).

3. Results and discussion

The PALS spectra of the samples taken before and after the synthesis, as well as after the calcinations have been analyzed using the LT 9 fitting program [23]. The lifetime and intensity values of the long-lived components

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(τ_3 , I_3 and τ_4 , I_4) were obtained using the best fits as shown in Table. They correlate to the *o*-Ps annihilation in voids inside the structure. The sizes of those voids can

be determined using the Tao–Eldrup model for lifetimes up to 10 ns [24, 25] or using modified the Tao–Eldrup model for longer lifetimes [26].

TABLE

The lifetime and intensity values of the long-lived components (τ_3 , I_3 and τ_4 , I_4) of the samples prepared from: (a) the original gel, (b) modification-1, and (c) modification-2. Errors in parenthesis.

Sample	(a) original gel		(b) modification-1		(c) modification-2	
	τ_3 [ns], I_3 [%]	τ_4 [ns], I_4 [%]	τ_3 [ns], I_3 [%]	τ_4 [ns], I_4 [%]	τ_3 [ns], I_3 [%]	τ_4 [ns], I_4 [%]
before synthesis	4.05(0.02), 9.4(0.2)	28.3(0.3), 4.62(0.08)	3.21(0.01), 11.6(0.1)	24(1), 0.68(0.01)	4.28(0.01), 10.75(0.03)	25.9(0.5), 2.02(0.02)
after synthesis	3.70(0.02), 10.3(0.1)	16.1(0.3), 1.08(0.02)	3.788(0.009), 14.47(0.03)	29(1), 0.80(0.01)	3.50(0.02), 11.7(0.1)	27(1), 0.74(0.02)
after calcination	4.2(0.2), 3.86(0.08)	31.1(1.7), 11.0(0.4)	4.2(0.2), 1.81(0.03)	36.0(0.3), 11.20(0.07)	3.84(0.05), 2.46(0.02)	34.6(0.05), 12.47(0.02)

The presence of the mesoporous template in the samples before synthesis is shown in the FTIR spectra at the bands of ≈ 2920 , 2850, 1483, and 730 cm^{-1} [27] (Fig. 1). In the PALS spectra, the third lifetime components, τ_3 , with values from 3.21 to 4.28 ns and I_3 of approximately 10% (Table), are assigned to the *o*-Ps annihilation in a mesoporous template interior [19, 20]. The lower τ_3 values for modification-1 compared to the other samples could be due to a higher packing parameter of the mesoporous template which in turn are caused by a higher charge density of the silica species (formed during RT ageing of the modified original gel [21, 28] that surround the template [29]). The τ_4 values in all samples before synthesis range from 24 to 28 ns, with low I_4 values (Table). They can be ascribed to the voids between the aggregates of the mesoporous template and the silica species.

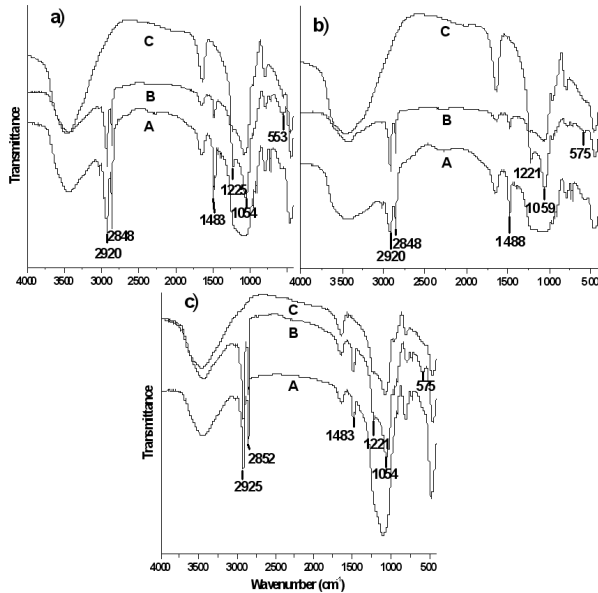


Fig. 1. FTIR spectra for the samples prepared from: (a) the original gel, (b) modification-1 and (c) modification-2. Spectrum A — sample before synthesis, spectrum B — sample after synthesis and spectrum C — sample after calcination.

In the samples after synthesis, the τ_3 values, connected to the template presence, are from 3.5 to 3.7 ns and the corresponding I_3 values remain high (Table). This finding is consistent with the polymerisation of silicate species and thickening of the wall around the template micelle during synthesis [30, 31], which reduces the free space in the template interior and consequently the τ_3 values. At the same time, inter-aggregate condensation takes place [29], which influences the τ_4 values (Table) while the intensity, I_4 , values remain low.

The FTIR spectra of the samples after synthesis and calcination (Fig. 1) show several characteristic features. The changes of the bands at ≈ 1220 and ≈ 1050 cm^{-1} indicate the formation of an ordered zeolite structure [21, 30]. The band at ≈ 570 cm^{-1} indicates the presence of structural units (double five rings — D5R) characteristic of a pentasil zeolite structure [28, 32].

After the calcinations, the τ_3 values of the samples are from 3.8 to 4.2 ns, whereas the I_3 values decrease as compared to the I_3 values in samples after the synthesis (Table). At the same time, both τ_4 and I_4 values increase (Table). The decrease in I_3 values is connected to the template removal from the samples, which is also shown by the disappearance of the bands in the FTIR spectra characteristics for the template (Fig. 1, spectra C). However, some of the template is still present in the samples as indicated by the low I_3 values [20]. The sizes of the voids, which emerged after removing the template, are ≈ 2.2 nm as estimated from the τ_4 values.

The X-ray diffractograms of the calcined samples are shown in Fig. 2. Broad amorphous peaks are characteristic for all samples. Diffraction pattern characteristic for crystalline zeolite superimposed on the broad peak in the sample prepared from the original gel (Fig. 2, diffractogram A) imply zeolite structural features in the obtained material [33], whereas short range order in the other calcined samples, seen by FTIR, remain undetected (Fig. 2, diffractograms B and C).

4. Conclusion

Using PALS we have studied formation of mesoporous materials from zeolite precursors and mesoporous template. Long lived components, τ_3 and τ_4 , show presence

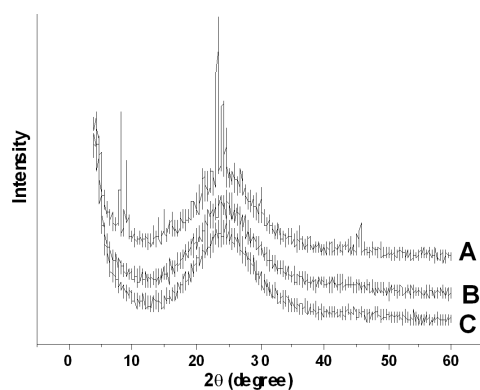


Fig. 2. X-ray diffractograms of calcined samples obtained by synthesis from: the original gel (diffractogram A), modification-1 (diffractogram B), and modification-2 (diffractogram C).

of the template and created voids by calcination, respectively. Following calcination, a decrease in I_3 and an increase in I_4 values show the removal of the mesoporous template. The sizes of voids formed after removal of the template and estimated from the τ_4 values are ≈ 2.2 nm. The FTIR and XRD results show presence of some zeolite structural units in the obtained materials. This leads to the conclusion that materials obtained by the applied synthesis procedure possess voids in mesosized ranges within a partial zeolite structure.

Acknowledgments

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