

## Non-thermal calcination by ultraviolet irradiation in the synthesis of microporous materials

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### Abstract

We describe a new photochemical method near room temperature conditions for the removal of organic structure-directing agents in the synthesis of microporous materials. The method relies on the exposure of the sample to short-wavelength ultraviolet (UV) radiation in air and the ozone environment generated by a medium pressure mercury lamp (184–257 nm). The generality of the approach has been confirmed using three test-cases of microporous materials: a high-silica synthetic zeolite, an aluminophosphate, and a Ge-substituted microporous silica. The structures and organic contents of the microporous materials before and after UV/ozone treatment were determined using a combination of X-ray diffraction, Fourier-transform infrared spectroscopy, thermogravimetry, and nitrogen adsorption isotherms. For all three cases, the UV/Ozone treatment allows complete removal of the organic template while retaining the inorganic framework. The overall integrity of the microporous materials was comparable to or better than for materials derived by thermal calcination. This method is applicable in making new materials from organic–inorganic precursors and holds promise for microporous thin films on thermally sensitive substrates and for controlled spatial patterning.

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### 1. Introduction

Microporous and mesoporous materials, displaying ordered arrangements of nanometer size pores, are generally synthesized using organic ions and surfactant molecules as structure-directing agents (SDA) or templates [1,2]. Examples include natural aluminosilicate zeolites, high silica zeolite-like materials, and MCM-type mesoporous materials [3]. There is growing interest

in making microporous materials that display novel, non-traditional inorganic compositions containing elements such as Ga, P, Ge, Co, and Zn in their frameworks [4]. Much of this interest stems from the realization that such mixed inorganic framework allow the creation of new framework types, larger ring structures and pore dimensions, or complex nanoscale topologies [5]. However, for such materials to be useful as catalysts, ion exchangers, sensors, or separation membranes, the organic molecules co-crystallized in the structure must be removed. For traditional microporous materials, this is most frequently achieved by thermal calcination at 400–600 °C, although in some cases, supercritical solvent extraction [6] has also been used. The newer classes of microporous materials with

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unusual compositions and frameworks are often quite fragile. Such materials often do not survive high-temperature calcination, collapsing to an amorphous phase of low surface area. To maintain open inorganic frameworks, a template removal method operating at or near room temperature is desirable.

Furthermore, several emerging applications (e.g., sensors, separation membranes, low dielectric constant materials, lasing media) of microporous materials require planar forms of these and other microporous materials [7]. Thus, there is interest in their design as thin films, membranes, and molecular layers on substrate supports. A major disadvantage of the direct synthesis of microporous materials on substrate surfaces is the need for calcination. The high temperature calcination process can induce large thermal stresses at the film–substrate interface. Moreover, high-temperature calcination processes are unsuitable for synthesizing microporous thin films on temperature-sensitive substrates, e.g., semiconductors, thin-metal film substrates, and organic materials.

Here we report the application of short-wavelength ultraviolet (UV) radiation to completely remove organic molecules from micropores near-room temperature conditions. The non-thermal calcination (NTC) process converts the organic to carbon dioxide, water, and nitrogen which escape the material surface and leave behind well-defined crystalline microporous materials displaying high surface areas.

## 2. Experimental

### 2.1. Materials

To demonstrate the NTC process, while simultaneously providing direct comparison with thermal calcination, we used three well-characterized material samples. These were a TPA-silicalite-1 (TPA = tetrapropylammonium) (structure code: MFI),  $\text{AlPO}_4\text{-5}$  aluminophosphate (structure code: AFI), and Ge-containing ITQ-7. Synthesis of the three test compounds followed previously published procedures [8–11]. Briefly, TPA-silicalite-1 (MFI zeolite) was synthesized [8] by reacting an initial synthetic mixture with the composition  $25\text{SiO}_2\text{:}480\text{H}_2\text{O:}9\text{TPAOH:}100\text{ethanol}$  at  $80^\circ\text{C}$  for 72 h. The synthetic mixture was prepared by vigorously stirring 119.10 g of 10% TPAOH solution (Fisher), 30.32 g of 40% TPAOH solution (Alfa), and 68.4 g of tetraethylorthosilicate (TEOS, Alfa) at room temperature for 2–3 h till homogeneous and optically clear.  $\text{AlPO}_4\text{-5}$  was similarly prepared [10] by reacting a synthetic mixture of composition  $1.5\text{ tripropylamine:Al}_2\text{O}_3\text{:P}_2\text{O}_5\text{:}40\text{H}_2\text{O}$  at  $150^\circ\text{C}$  for 48 h under an autogenous pressure in a Teflon-lined autoclave. Specifically, the initial mixture was prepared by adding 4.75 g tripropylamine to a pre-

hydrolyzed aqueous solution of 12 g aluminum isopropoxide slurry. After 10 min of vigorous stirring,  $\text{H}_3\text{PO}_4$  was dropped slowly into the mixture. Tripropylamine served as a structure-directing agent for  $\text{AlPO}_4\text{-5}$  whereas tetrapropylammonium hydroxide was used for the MFI zeolite. Ge-substituted ITQ-7 (Instituto de Tecnología Química-Siete, structure code: ISV) exhibiting a Si/Ge-ratio of 5 was synthesized [11] with a material composition of  $0.833\text{SiO}_2\text{:}0.167\text{GeO}_2\text{:}0.50\text{C}_{14}\text{H}_{26}\text{NOH:}0.5\text{HF:}3\text{H}_2\text{O}$  where  $\text{C}_{14}\text{H}_{26}\text{NOH}$ , 1,3,3-trimethyl-6-azoniumtricyclo [3.2.1.4<sup>6,6</sup>] dodecane hydroxide, is the SDA.

### 2.2. Non-thermal calcination process

Our nominally room-temperature photochemical calcination (we call this class of reactions non-thermal calcination, NTC) exposes the as-synthesized microporous materials to ozone-generating short-wavelength UV radiation ( $\lambda = 184\text{--}257\text{ nm}$ ). The UV radiation was produced using a medium-pressure Hg-discharge grid lamp (UVP, Inc., Upland, CA) in a quartz envelope, and maintained in a closed chamber in a chemical hood. 5–10 mg of sample material was spread evenly on 5" silicon wafers or aluminum foils inside the UV-chamber. The samples were maintained 2–3 mm below the lamp surface and the exposure time was varied between 30 and 60 h. The exposure time and the exposure geometry have not been optimized. While the UV treatment was performed at room temperature, local temperature of the sample during the process increased to  $50\text{--}70^\circ\text{C}$ . Thermal calcination of the as-prepared materials at  $550^\circ\text{C}$  for  $\sim 10\text{ h}$  in air was also carried out to enable direct comparison of the two SDA removal processes.

### 2.3. Characterization

All materials were characterized before and after calcination (thermal and UV/Ozone treatment) using a combination of powder X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). Pore characteristics of calcined and UV/ozone treated or NTC samples were characterized using nitrogen adsorption porosimetry.

Powder XRD experiments were performed on an Inel X-ray diffractometer operated at 30 kV and 30 mA using Ni-filtered  $\text{Cu K}_\alpha$  radiation ( $\lambda = 1.54056\text{ \AA}$ ). Data were collected in the  $2\theta$  range of  $5\text{--}50^\circ$ . FTIR transmission spectra were obtained using an air-purged, Fourier transform spectrophotometer (Equinox 55, Bruker Optics) operating at  $2\text{ cm}^{-1}$  resolution with an unpolarized beam striking the sample at normal incidence. The beam diameter was controlled at 8 mm by an aperture placed adjacent to the sample. The resulting interferograms, obtained by adding 100 scans, were Fourier transformed with triangular apodization to obtain spectral traces.

The sample consisted of essentially transparent pellets prepared by pressing a mechanically homogenized mixture of the dried sample with nominally dry pure KBr in calculated quantities. The spectra were referenced against that of air or blank KBr pellets under identical spectrometer conditions and geometry. Thermal analyses (TGA/DSC) were performed in an argon atmosphere on a Netzsch STA 449C apparatus. Temperature and sensitivity calibrations were performed with indium, bismuth, zinc, aluminum and gold standards supplied with the calorimeter. The heating rates were 5, 10, or 20 °C/min. The temperature and the heat of the first peak seen were calculated from the average values of 5–6 runs. Gases evolved during thermal analysis were analyzed by a Bruker Equinox 55 FTIR spectrometer, which was directly coupled with TG/DSC by a heated transfer line kept at 150 °C. FTIR spectra of evolved gases were collected in a range from 400 to 4000  $\text{cm}^{-1}$  at a resolution of 4  $\text{cm}^{-1}$ . A baseline correction was made before each run. A Micromeritics ASAP 2010 porosimeter operating at  $-196\text{ }^\circ\text{C}$  (77 K) was used to obtain nitrogen adsorption isotherms. Samples were outgassed at 225 °C for 12 h under ultra-high-purity He. Liquid nitrogen was used as a coolant over a P/P(sat) range of 0.00025–1.0. Typically, 30 s of equilibration time was used and adsorption/desorption isotherm cycles measured. Surface area was estimated by using the Brunauer–Emmet–Teller (BET) equation; and the pore size was calculated by modeling the pore as cylinders with the hydraulic radius  $r = 2V/S$ , where  $V$  is the pore volume and  $S$  is the surface area.

### 3. Results and discussion

#### 3.1. Non-thermal calcination of silicalite-1 and an auminophosphate zeolite

It is now well established that when TPA-silicalite-1 and  $\text{AlPO}_4\text{-5}$  aluminophosphate materials are thermally calcined, they retain their crystallinity, lose the SDA, and exhibit highly accessible porosity, thereby yielding well-characterized microporous molecular sieve materials [8,10]. Remarkably similar changes are observed under NTC.

Characterization of the template organic phase was performed primarily using FTIR spectroscopy. Fig. 1 shows FTIR traces for as-prepared, thermally calcined (tc), and NTC for TPA-silicalite-1 and  $\text{AlPO}_4\text{-5}$ . The presence of SDA molecules in the as-synthesized samples is directly discerned by a number of peaks. Note the SDA peaks with maxima at 2883, 2943, and 2981  $\text{cm}^{-1}$  for the TPA-silicalite-1 and a series of overlapping peaks with maxima at 2681, 2956, and 3005  $\text{cm}^{-1}$  for the  $\text{AlPO}_4\text{-5}$  in the high frequency region (2700–3100  $\text{cm}^{-1}$ ) of the spectra. These peaks can be

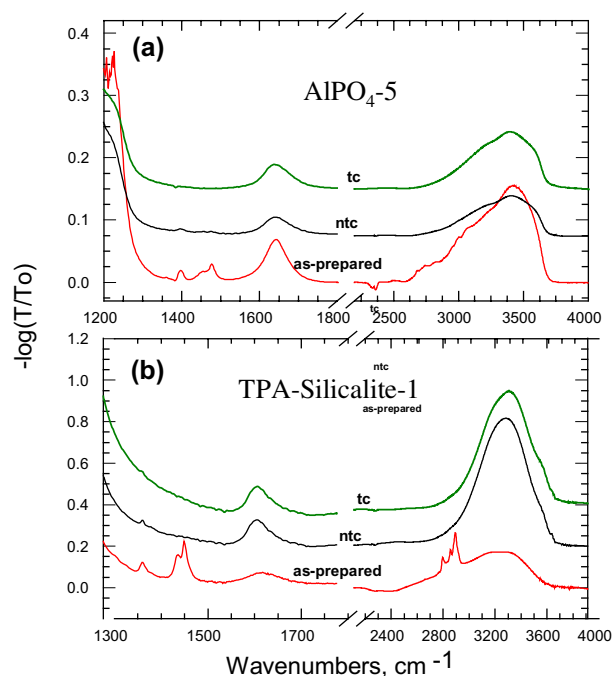


Fig. 1. Fourier-transform infrared transmission spectra of pressed KBr pellets containing measured quantities of as-prepared, thermally calcined, and photochemically treated (NTC). (a)  $\text{AlPO}_4\text{-5}$  and (b) TPA-Silicalite-1.

straightforwardly assigned to modes due to methylene ( $-\text{CH}_2-$ ) and methyl ( $-\text{CH}_3$ ) C–H vibrations [12]. The lower frequency (1300–1600  $\text{cm}^{-1}$ ) region of the spectra show methyl bending mode in the 1460–1470  $\text{cm}^{-1}$  region [12]. For the TPA-silicalite-1, a doublet with maxima at 1460 and 1474  $\text{cm}^{-1}$  is observed. A broad envelope with a maximum at 1478  $\text{cm}^{-1}$  is seen for  $\text{AlPO}_4\text{-5}$ . In the spectra for the thermally calcined samples and UV exposed NTC samples, these peaks are noticeably absent, suggesting essentially complete removal of the SDA. (Residual organics must be well below 1% of the original content.) There is a weak, but distinct, feature between 3700 and 3740  $\text{cm}^{-1}$  in the NTC TPA-silicalite-1 spectrum within the broad envelope. This peak can be resolved by Fourier deconvolution in the spectrum for NTC  $\text{AlPO}_4\text{-5}$  sample as well, but the raw spectrum collected at 2  $\text{cm}^{-1}$  resolution does not show a well-resolved peak on visual inspection. These features are probably due to the formation of non-acidic isolated silanol, Si–OH, groups [13]. The presence of these isolated silanols has been previously suggested to be associated with the SDA-free pore walls [14]. In this regard, the presence of vibrational absorption modes due to isolated silanol is further consistent with the removal of SDA. Additional support for the essentially complete removal of SDA was obtained by the carbon analysis. The initial C contents for  $\text{AlPO}_4\text{-5}$  and TPA-silicalite-1 were 4.9% and 10.3%, respectively, for as-synthesized samples. These decreased to 0.036%

( $\text{AlPO}_4\text{-5}$ ) and 0.046% (TPA-silicalite-1) upon NTC, comparable to the values of 0.039% and 0.050%, respectively, for thermal calcination.

The crystallinity and phase stability of the inorganic framework were assessed using powder XRD measurements. Representative traces for TPA-silicalite-1 and  $\text{AlPO}_4\text{-5}$  as-synthesized, thermally calcined, and NTC samples are shown in Fig. 2. The patterns for the as-synthesized TPA-silicalite-1 and  $\text{AlPO}_4\text{-5}$  show a series of well-resolved intense peaks. These peaks can be readily assigned to the ( $hkl$ ) reflections for the Pnma orthorhombic and P6cc hexagonal symmetries, respectively, in good agreement with previous reports [15,16]. Thus, the as-prepared solids are fully crystalline as revealed by the presence of all characteristic peaks. There is no evidence for the presence of amorphous material which would give a broad “hump” to the patterns below  $30^\circ 2\theta$ . After the thermal calcination or NTC, these peaks remain, suggesting that the microporous materials retain their crystallinity and phase upon calcination. A detailed comparison of the patterns for NTC and thermally calcined materials confirms that the retention of crystalline order of the

inorganic oxide frameworks upon NTC is quantitatively comparable to that of thermally calcined samples.

Nitrogen adsorption isotherm measurements, shown in Fig. 3, were used to characterize sample porosities. The data indicate type I isotherms, typical of microporous materials, with little or no hysteresis. BET surface-areas for NTC samples are  $501\text{m}^2\text{g}^{-1}$  for TPA-silicalite-1 and  $310\text{m}^2\text{g}^{-1}$  for  $\text{AlPO}_4\text{-5}$ . By comparison, thermally calcined samples have surface areas of  $501\text{m}^2\text{g}^{-1}$  and  $240\text{m}^2\text{g}^{-1}$ , respectively. Thus, the surface areas of UV irradiated organic-free NTC samples are as high or higher than those of SDA-free materials produced by conventional thermal calcination.

The thermal behavior of NTC samples is also comparable to that of thermally calcined samples. For both  $\text{AlPO}_4\text{-5}$  and TPA-silicalite-1, NTC samples show less than 2% mass loss in thermogravimetry (data not shown). These losses occur mostly below  $170^\circ\text{C}$ , indicating the loss of physically adsorbed water. This is in good agreement with the behavior of thermally calcined samples [8,10].

### 3.2. Non-thermal calcination of a Ge-doped ITQ-7 microporous material

An important practical feature of NTC is that SDA removal occurs near room temperature. Therefore, template-free molecular sieve materials can be designed whose frameworks tend to become unstable or even collapse during the aggressive thermal calcination process. To illustrate this feature, we studied NTC of a germanium-substituted ITQ-7, an example of a new class of silicate–germanate molecular sieves [17]. The material is of particular interest for its unique topology: it presents a very low-density inorganic framework with a three-dimensional system of large pores containing double four-membered rings. Removal of the SDA by thermal calcination is known to destabilize its inorganic framework, possibly because of its high sensitivity to moisture absorption from air [18]. Recently, we have observed that, when carefully optimized, thermal calcination can preserve the structure of ITQ-7 upon SDA removal [19]. However, absorption of water under ambient conditions gradually degrades its inorganic framework, which loses crystallinity in several days.

Comparison of the FTIR spectra for as-prepared, thermally calcined using the optimized approach as above [19], and NTC samples shown in Fig. 4 confirms the effectiveness of UV irradiation. The C–H stretching vibrational modes in the  $2700\text{--}3100\text{cm}^{-1}$  region, assigned to the methylene and methyl C–H stretching vibrations for SDA, are clearly visible in the as-synthesized sample. Upon exposure to UV light during NTC, these features became undetectable, confirming the loss of SDA. Thermally calcined samples show similar behavior. A noticeable difference between the thermally calcined and NTC ITQ-7 spectra is the presence of a

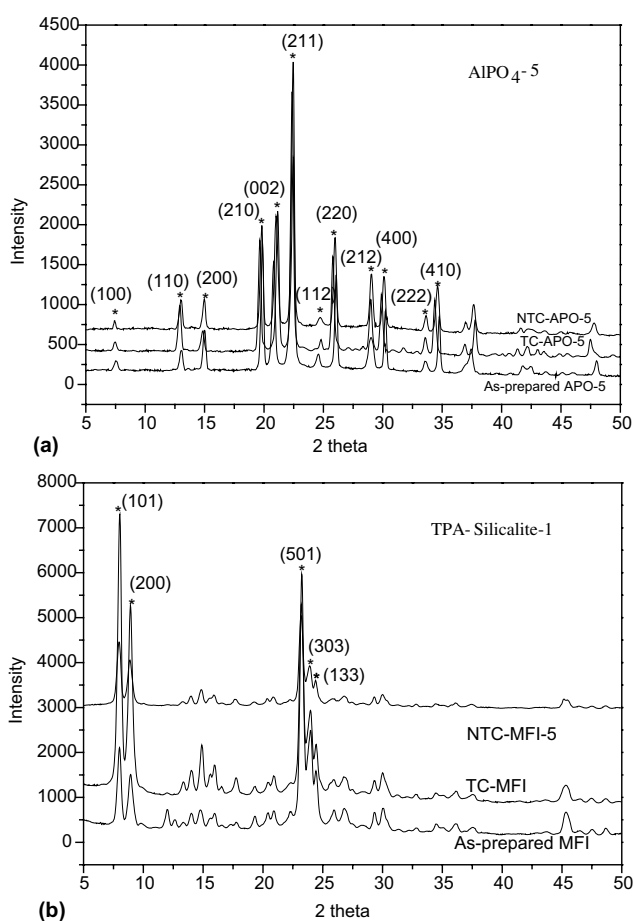


Fig. 2. X-ray diffraction patterns of as-prepared, thermally calcined, and photochemically treated (NTC). (a)  $\text{AlPO}_4\text{-5}$  and (b) TPA-silicalite-1.

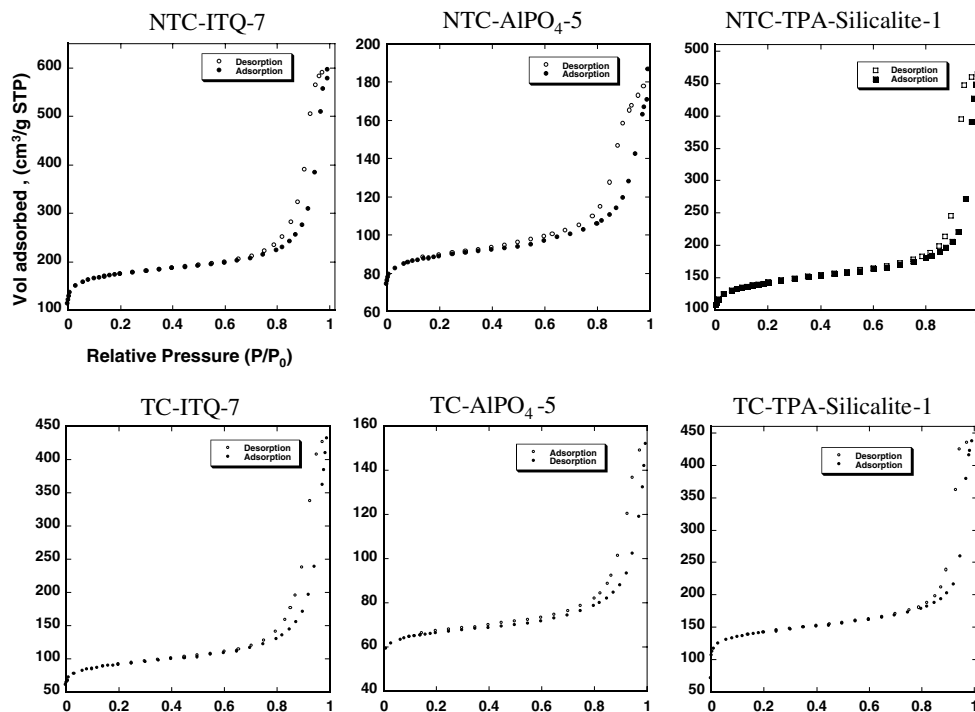


Fig. 3. Nitrogen adsorption isotherms for  $\text{AlPO}_4\text{-5}$  and TPA-Silicalite-1.

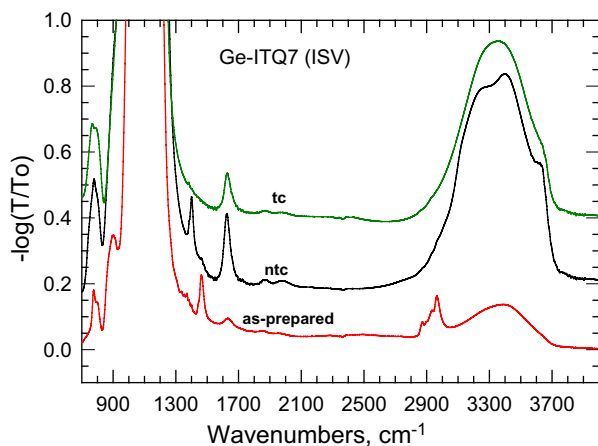


Fig. 4. Fourier-transform infrared transmission spectra of pressed KBr pellets containing comparable quantities of as-prepared, thermally-calcined, and photochemically treated (NTC) Ge-substituted ITQ-7.

strong peak at  $1380\text{ cm}^{-1}$  in the NTC spectrum. We currently do not understand the origin of this peak. Systematic study of variously doped ITQ-7 samples will be needed to provide a proper assignment. BET isotherm data (Fig. 3) however reveal a difference: accessible porosity for thermally calcined samples is much lower ( $319\text{ m}^2\text{ g}^{-1}$ ) than that ( $612\text{ m}^2\text{ g}^{-1}$ ) for NTC.

This difference in porosity of NTC and thermally calcined samples can be better understood by examining the crystallinity changes that attend NTC and thermal calcination. XRD patterns for as-synthesized, thermally

calcined and NTC ITQ-7 are shown in Fig. 5. The XRD data for the as-synthesized ITQ-7 (inset in Fig. 5) are comparable to that reported previously [18] and suggests high crystallinity. Broad features observed for thermally calcined ITQ-7 (Fig. 5(a)) indicate that the crystallinity is significantly lowered during thermal calcination. Moreover, the broadening of the XRD features became even more pronounced when thermally calcined samples were exposed to air or moisture for 7 days (Fig. 5(b)), suggesting further deterioration in crystallinity, eventually

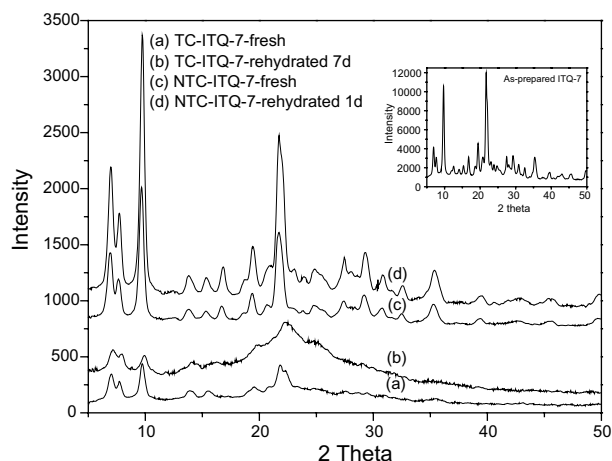


Fig. 5. X-ray diffraction patterns of thermally calcined and photochemically treated Ge-substituted ITQ-7 upon (a) calcination and (b) calcination followed by laboratory air exposure for 7 days. Inset shows the pattern for as-prepared ITQ-7 before calcination.

leading to complete framework collapse (Fig. 5(b)). In sharp contrast, the diffraction pattern in Fig. 5(c) suggests that the NTC sample retains significantly higher crystallinity upon SDA removal and does not collapse even upon extended exposure to air at about 50% relative humidity (see Fig. 5(d)).

### 3.3. Plausible mechanism of photochemical calcination

It is now well-established from studies on a diverse range of materials that the mechanism by which short-wavelength UV radiation destroys the organics involving a complex set of photosensitized oxidation processes [20]. The simplest description of the overall process involves three overlapping photo-induced chemical reactions. First, UV light with a wavelength below 245.4 nm (optimally at  $\lambda = 184$  nm) facilitates the dissociation of oxygen (from the ambient) to produce ozone and atomic oxygen. Simultaneously, the 253.7 nm line emitted by the same lamp excites and/or dissociates the organic matrix, thereby producing activated species, such as ions, free radicals, and excited molecules. Finally, the activated organic species are readily attacked by atomic oxygen and ozone synergistically to form simpler volatile (or removable) organic products, such as CO<sub>2</sub>, H<sub>2</sub>O, and N<sub>2</sub> which escape the sample interior. Recent reports by Keene et al. [21] and Clark et al. [22] suggest that the ozone produced by UV light can be used to extract surfactant microphases in the synthesis of MCM-41 mesoporous materials and mesoporous thin films. In a more recent study employing direct ozonation, Buchel et al. [23] suggest that the process is generally inefficient and requires aqueous phase suspension of the as-synthesized MCM-41 to effectively remove the organic. While the detailed mechanistic basis for the success of NTC is not known, it is clear that the simultaneous presence of UV light which excites the organic molecule and the ensuing generation of activated oxygen and ozone are needed for effective photocalcination.

## 4. Conclusions

Non-thermal calcination (NTC) of microporous materials promises to be an enabling technology for maintaining crystalline inorganic frameworks that are intolerant of high temperature calcination, as well as for designing potentially new classes of microporous materials that can not be prepared using thermal calcination. Moreover, the approach is directly applicable to molecular sieve layers and thin films where spatial localization of the calcination process can be conveniently achieved to produce microporous material functionality in a surface patterned architecture. These investigations are currently being pursued in our laboratories. Furthermore, NTC offers a general approach

to removing organics from other sol-gel and hydrothermally synthesized advanced materials, such as octahedral molecular sieves, oxide nanoparticles, and organic-inorganic composites. Minimizing structural collapse, this method may yield new classes of materials.

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