Use of Radiofrequency Plasma for Low-temperature Calcination of Zeolites

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A dry air radiofrequency plasma is shown to be suitable for calcining zeolites at low temperature.

Applications of radiofrequency plasmas include manufacturing of integrated circuits[1] and sample preparation for electron microscopy. Radiofrequency plasma is generated by the action of a radiofrequency discharge on a rarefied gas; a dry air radiofrequency plasma is a strong oxidant, removing combustibles under well defined conditions at low temperature.[2]

Zeolites are exposed to thermal treatment at elevated temperature for various purposes, such as template removal from as-synthesized materials and activation in catalyst preparation. At the temperatures applied, extensive reactions such as ultrastabilisation,[3] cation redistribution,[4] and de- and re-alumination[5] may occur in the zeolite.

We have explored the application of a radiofrequency plasma treatment for low temperature oxidation of combustibles in various zeolites. We have established that such treatment does not impair the zeolite structure, by subjecting a sample of hydrated zeolite NaA to 3 h treatment with a 30 W 0.2 Torr dry air plasma. The water lost during treatment was fully readsorbed during exposure to ambient air. Moreover, by exposing various sealed capillaries containing low-melting compounds to a dry air plasma we were able to estimate that the temperature in the plasma used in our experiments was approximately 45 °C.

The mildness of the plasma treatment was further demonstrated by the unchanged powder *X*-ray diffraction pattern of as-synthesized zeolite Ω (prepared as example A6 of ref. 6) after 76 h exposure (30 W, 2.0 Torr). Although tetramethylammonium occluded in the gmelinite cages is difficult to remove by conventional calcination,[7] the decrease in wavenumber of the C–H bending i.r. vibration at 1485 cm^{-1} shows that the plasma has removed most of the template.

Removal of the NH_3 deformation band (1410 cm^{-1}) in the i.r. spectra of NH_4 mordenite and $Pt(NH_3)_4$ mordenite (prepared by ion-exchange as described in ref. 8) is accomplished at ±45 °C after 27 h plasma treatment (30 W, 1 Torr). Usually these transformations require careful calcination at temperatures up to 600 °C.

Silicalite prepared according to Wey *et al.*[9] was treated for 12 h in a 30 W 1 Torr dry air plasma. The product was examined by thermogravimetric analysis, i.r. spectroscopy, and *X*-ray diffraction. Thermogravimetry showed the treated

sample to be free of combustibles. The ratio of the 550 and 450 cm^{-1} i.r. absorptions[10] as well as the *X*-ray diffraction pattern showed that the crystallinity of the sample is not affected by the plasma treatment. I.r. analysis also showed the absence of C–H vibrations at 3100—2700 cm^{-1} and fine structure in the Si–OH and Si–F vibration region (1000—850 cm^{-1}).[11] The former vibrations are present in as-synthesized silicalite, and are due to the tetrapropylammonium template. The fine structure is absent in high-temperature-calcined silicalite and present in as-synthesized material. These results indicate that the low-temperature plasma treatment has removed the template without rearranging the remaining surface to an appreciable extent.

Moreover, *X*-ray diffraction confirms that removal of the template results in a structure transition from orthorhombic to monoclinic.[12] Accordingly we conclude tentatively that dry air plasma treatment and conventional calcination affect long-range ordering similarly, but that, in contrast to heat treatment, plasma treatment leaves the local ordering unaffected and allows investigation of hitherto unaccessible transient states.

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