Looking Beyond Crystallinity of Zeolites with Solid-State NMR

Ana Palčić[1]
[1]*Laboratory for Synthesis of New Materials, Division of Materials Chemistry, Ruđer Bošković Institute, Bijenička cesta 54, 10000 Zagreb, Croatia*

Thermomilling combines high-frequency milling with simultaneous controlled heating and offers an alternative approach to zeolite synthesis. While powder X-ray diffraction provides essential information on phase composition and reaction kinetics, zeolite materials of comparable long-range crystallinity may differ considerably at the local structural level. Solid-state NMR spectroscopy is thus particularly important for establishing how thermomilling affects the environments of framework atoms and whether their formation under such conditions yields materials structurally equivalent to those obtained by oven treatment. Herein, thermomilling was applied to the interzeolite conversion and direct synthesis from chemicals. ^{29}Si and ^{27}Al MAS NMR, complemented by ^{1}H–^{29}Si cross-polarization experiments, revealed differences in framework ordering, Al environments and H–Si spatial proximities. The results depend on the particular synthesis system: in some cases thermomilled and oven-derived materials exhibit similar local structures, whereas in others clear differences persist despite formation of the same framework. These findings demonstrate that evaluating thermomilling solely through accelerated appearance of diffraction peaks provides an incomplete description of the process. Combining diffraction with solid-state NMR data enables understanding zeolite formation across different structural length scales and provides insight into how mechanically intensified synthesis influences framework organization, defects and the local environments ultimately governing zeolite properties.

Short bio:

Palčić Ana is a senior research associate at the Ruđer Bošković Institute in Zagreb, Croatia, focused on zeolite synthesis and characterization: zeolite formation, nanosized zeolites, interzeolite conversion and mechanochemical synthesis, with emphasis on structure–property relationships. She received her PhD in Chemistry from the University of Zagreb and conducted postdoctoral research at ENSICAEN, University of Caen, France. At present she is president of the Croatian Zeolite Association and a Board Member of the Federation of European Zeolite Associations.