Structure and dynamics of glass forming Metal Organic Frameworks: NMR study of Zeolitic Imidazolate Framework ZIF-62

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Abstract

Zeolitic Imidazolate Frameworks (ZIFs), a subset of microporous Metal-Organic Frameworks (MOFs), are three-dimensional polymeric networks built from inorganic metal-ion nodes, such as Zn2+, interconnected by organic linkers. In this family, the ZIF-62 compounds are heterolinked by imidazole (C3H3N2-) ("Im") and benzimidazole (C7H5N2–) ("bIm") anions, with various Im to bIm ratio. Hence, they have an intrinsically disordered structure in their crystalline form since bIm is statistical distributed around the zinc cations. ZIF-62 compounds are one of few ZIFs that can form glasses upon cooling from their melts. These glasses have found applications as membranes for gas separation owing to their significantly higher porosity than their inorganic cousins. The moulding ability of their glassy forms enables a wide range of applications when combined with other compositions to form property-tuneable composite materials.

Solid-state NMR spectroscopy is particularly well suited to study the local structure of ZIFs, both in the crystalline and in the melted states. In the present work, we followed *ex-situ*, the structure transformation(s) of ZIF-62 occurring as a function of composition using magic-angle spinning (MAS) NMR spectroscopy, applying a variety of one-dimensional and two-dimensional experiments involving 1H, 13C, 15N and 67Zn nuclei. Although extremely challenging, we also performed *in-situ* high-temperature MAS NMR experiments, from low temperature (-173◦C) to the molten state (500◦C).

The ensemble of data, associated with NMR lineshape simulations, highlight two types of movements of the Im organic linker at frequencies ranging from around 10 MHz to around 80 MHz and dependent upon composition. A pre-fusional phenomenon is also observed around Tg. Yet no evidence of bond breaking mechanism of melting is evidenced, but a progressive "softening" of the network constrained by steric effects. This study shed some light, for the first time, on the dynamics taking place in those MOFs and hence their peculiar mechanisms of melting and glass formation.

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