

## $^{27}\text{Al}$ solid-state NMR studies of zirconocene/MAO polymerization catalysts

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Single site homogeneous and heterogeneous metallocene catalysts used for olefin polymerization are of great value in many industrial processes [1]. However, it must be noted that these catalysts are not efficient polymerization catalysts unless they are first activated by a co-catalyst [2].

In 1980, Sinn discovered that the controlled addition of water to a mixture of  $\text{Cp}_2\text{ZrMe}_2$  and trimethylaluminum [TMA,  $\text{AlMe}_3$ ] created a highly active system for ethylene polymerization [3]. It is widely known that the hydrolysis of TMA leads to the creation of a co-catalyst, methylaluminoxane [MAO,  $(\text{AlOMe})_n$ ], which can then interact with  $\text{Cp}_2\text{ZrMe}_2$  to form an active catalytic system. Despite the importance of  $\text{Cp}_2\text{ZrMe}_2/\text{MAO}$  adducts to industrial polymerization processes, little is known regarding the role of MAO in these systems and why such a large ratio of MAO (Al:metallocene ratio of up to 10000:1) is needed to produce highly active catalysts [1].

Previous  $^{27}\text{Al}$  SSNMR studies have been undertaken in an attempt to determine the structure of MAO; however, the results were inconclusive [4]. It has been proposed that MAO consists of a multitude of cage type structures in which there are four-coordinate aluminum atoms bridged by three-coordinate oxygen (Figure 1) [6, 7]. Our  $^{27}\text{Al}$  static spectrum of MAO at 9.4 T (not shown) reveal a chemical shift of 100 ppm which is indicative of a four-coordinate aluminum center, as well as molecular level disorder owing to the presence of many different cage structures.  $^{27}\text{Al}$  MQMAS spectra of MAO acquired at 21.1 T reveal the presence of two distinct  $^{27}\text{Al}$  resonances (Figure 2a). The  $^{27}\text{Al}$  MQMAS data, in conjunction with DFT calculations (not shown), have enabled us to assign the resonances to

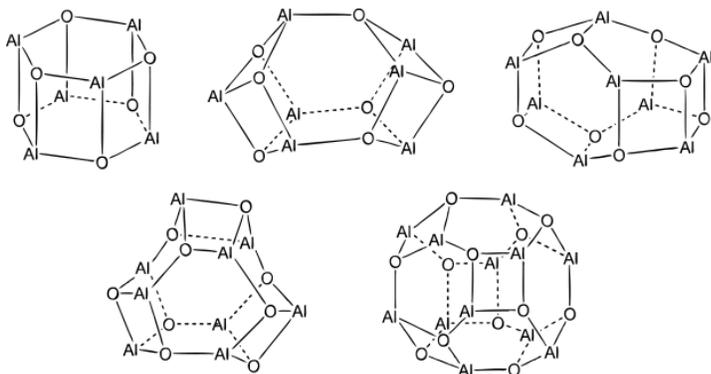


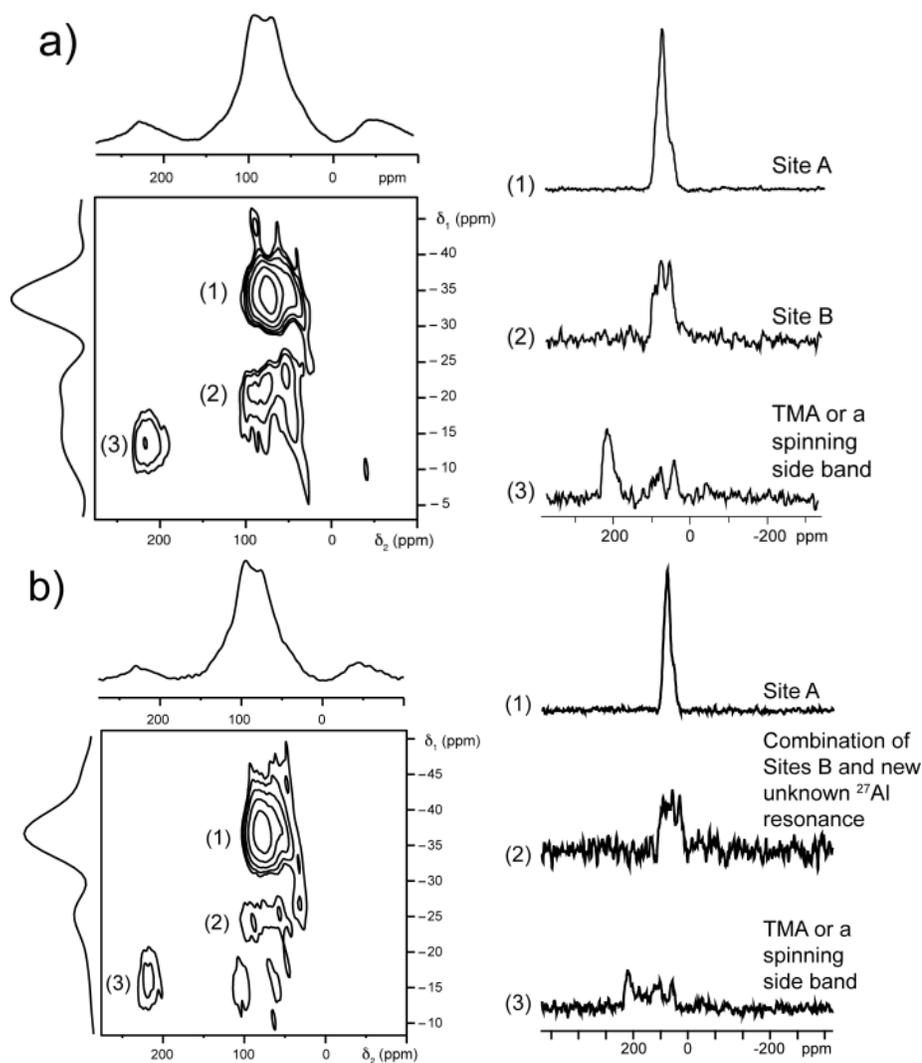
Figure 1: A selection of the proposed cage structures for MAO.

an aluminum in an environment that does not exhibit an appreciable amount of ring strain (Site A) and an aluminum in a ring strained environment (Site B). The  $^{27}\text{Al}$  MQMAS spectra of  $\text{Cp}_2\text{ZrMe}_2/5\text{MAO}$  (Figure 2b) reveal a change at the site assigned to an aluminum in a ring strained environment (Site B), when compared to the MQMAS spectra of pure MAO, suggesting that this type of site may be responsible for the

activation of  $\text{Cp}_2\text{ZrMe}_2$  to become an efficient polymerization catalyst. We are currently applying further  $^{27}\text{Al}$ ,  $^{13}\text{C}$ , and  $^1\text{H}$  NMR experiments, as well as first principles calculations, to investigate the nature of the interaction between MAO and  $\text{Cp}_2\text{ZrMe}_2$ . It is hoped that this will aid in the future rational design of effective polymerization catalysts.

#### References

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**Figure 2:** Conventional  $^{27}\text{Al}$  (21.1 T) MAS NMR spectra, triple quantum MAS NMR spectra, and corresponding isotropic projections of (a) MAO and (b)  $\text{Cp}_2\text{ZrMe}_2/5$  MAO. The spectra were recorded using a z-filtered MQMAS pulse sequence [5]. Also shown are the lineshapes obtained by taking F1 cross sections corresponding to each site. The MAS rate was 31.25 kHz.