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A systematic computational study of electronic effects on hydrogen sensitivity of olefin polymerization catalysts

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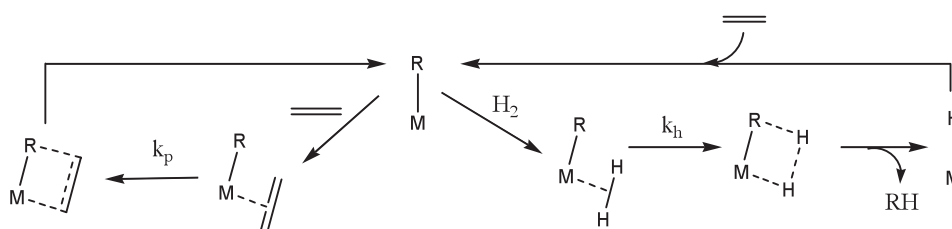
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Abstract

One of the important product parameters of polyolefins is their molecular weight (distribution). A common way to control this parameter is to add molecular hydrogen during the polymerization, which then acts as a chain transfer agent.

The factors governing the hydrogen sensitivity of olefin polymerization catalysts are poorly understood and have attracted little attention from computational chemists. To explore the electronic factors determining hydrogen sensitivity we performed density functional calculations on a wide range of simple model systems including some metallocenes and a few basic models of heterogeneous catalysts. As a quantitative measure for hydrogen sensitivity we used the ratio of (i) the rate constant for chain transfer to hydrogen to (ii) the rate constant for ethene insertion, k_h/k_p (see the scheme below), and as a measure of electrophilicity we used the energy of complexation to the probe molecule ammonia.



For isolated species in the gas phase, complexation energies appear to dominate the chemistry. Ethene complexes more strongly than hydrogen and with increasing electrophilicity of the metal centre this difference grows; the hydrogen sensitivity decreases accordingly. Although many factors (like catalyst dormancy and deactivation issues) complicate the comparison with experiment, this result seems to agree both in broad terms with the experimental lower hydrogen sensitivity of heterogeneous catalysts, and more specifically with the increased hydrogen sensitivity of highly alkylated or fused metallocenes. The opposite conclusion reached by Blom (see Blom *et al* 2002 *Macromol. Chem. Phys.* **203** 381–7) is due to the use of a very different measure of electrophilicity, rather than to different experimental data.