

P08

# Understanding Structure and Properties of MgCl<sub>2</sub> Supported Ziegler-Natta Nanoclusters by DFT, Spectroscopy and Machine Learning: How Modelling Uncovers the Origin of Industrial Catalysis

Maddalena D'Amore<sup>1\*</sup>, Gentoku Takasao<sup>2</sup>, Hiroki Chikuma<sup>2</sup>, Toru Wada<sup>2</sup>, Toshiaki Taniike<sup>2\*</sup>, Fabien Pascale<sup>3</sup>, and Anna Maria Ferrari<sup>1</sup>

<sup>1</sup>Dipartimento di Chimica, Università di Torino, Italy

<sup>2</sup>Graduate School of Advanced Science and Technology, Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Nomi, Ishikawa, 923-1292, Japan

<sup>3</sup>Université de Lorraine - Nancy, CNRS, Laboratoire de Physique et Chimie Théoriques, Vandoeuvre-les Nancy

\*Corresponding author

## ABSTRACT

MgCl<sub>2</sub>-supported Ziegler-Natta (ZN) catalysts for olefin polymerization are intrinsically complex multi-component systems, whose composition is the result of a long optimization process, mostly achieved in an empirical manner, either through a trial and error approach or through the more modern high-throughput screening of all the possible parameters. As it happens in many catalysts, nano-size and disorder are key features of ZN catalysts.<sup>i</sup> The structural and surface properties of MgCl<sub>2</sub> strongly depend on its activation that allows moving from the two crystalline polymorphs of MgCl<sub>2</sub> ( $\alpha$  and  $\beta$  phases) to a high-surface-area material actually suitable for catalytic applications ( $\delta$ -MgCl<sub>2</sub>). MgCl<sub>2</sub> as a support material offers unique advantages in terms of abundance and distribution of stereo-specific highly active sites<sup>ii</sup>, together with the regulation of the morphology of the produced polymer. The presence of multiple components interacting with each other and their sensitivity to moisture are the main difficulties encountered in the attempt to investigate these systems from an experimental point of view, which opened routes to quantum mechanics to provide insights into those complex systems.

The seminal MgCl<sub>2</sub> models as obtained from molecular mechanics in the 1980s presented the (110) and (104) lateral surfaces as the putative surfaces for the adsorption of monomeric TiCl<sub>4</sub> and dimeric species, respectively giving rise the first to a nonstereospecific site, whereas Ti<sub>2</sub>Cl<sub>8</sub> dimers would form on the (104) surface adducts with stereospecific properties. However, recent DFT studies have claimed the crisis of those models,<sup>iii,iv</sup> warning about the critical thermodynamic stability of Ti<sub>x</sub>Cl<sub>4x</sub> species on flat and regular MgCl<sub>2</sub> surfaces and moving towards a much more complex morphology of the  $\delta$ -MgCl<sub>2</sub> particles, where defective sites (such as steps, corners, and interfaces between two different surfaces) play a major role.

We recently investigated the effect of nanosize and structural disorder on the MgCl<sub>2</sub> support of Ziegler-Natta catalysts in terms of induced changes to its vibrational spectroscopic fingerprint by resorting to both periodic and cluster models. In particular, we adopted the inelastic neutron scattering (INS)<sup>v</sup> technique as a method for the characterization of materials with a certain degree



of defectivity and our investigation shows the central role of quantum mechanical simulations for a correct interpretation and valorization of the experimental INS spectra. Due to the nanosized nature of investigated catalysts, understanding the structure and properties of  $\text{MgCl}_2/\text{TiCl}_4$  clusters is a key to uncover the origin of Ziegler-Natta catalysis. In particular, vibrational spectroscopy can sensitively probe the morphology and active species of  $\text{MgCl}_2/\text{TiCl}_4$ . We determined vibrational spectroscopic fingerprints of  $50\text{MgCl}_2$  and  $50\text{MgCl}_2/3\text{TiCl}_4$  which were obtained by non-empirical structure determination based on an evolutionary algorithm and DFT.<sup>vi</sup> The adsorption of  $\text{CO}$ ,  $\text{TiCl}_4$  and  $\text{Ti}_2\text{Cl}_8$  dimers was also modelled on each of coordinatively unsaturated  $\text{Mg}^{2+}$  sites available for binding including so-called defect sites, which are likely present at the surface of activated  $\text{MgCl}_2$  nano-crystals and plausible sites for strong  $\text{TiCl}_4$  species adsorption. Vibrational analysis (IR and Raman) on plausible models of  $\text{TiCl}_4/\text{MgCl}_2$  clusters revealed that IR response is useful to distinguish between the different ways of binding of  $\text{TiCl}_4$  on different sites of adsorption, whereas Raman response provides a clear fingerprint of supported  $\text{TiCl}_4$  species.

## References

1. Zannetti, R.; Marega, C.; Marigo, A.; Martorana, A. J. *Polym. Sci. Part B Polym. Phys.* 1988, 26 (12), 2399–2412.
2. Correa, A.; Piemontesi, F.; Morini, G. and Cavallo, L. *Macromol.* 2007, 40, 9181-9189.
3. (a) Seth, M.; Margl, P.M.; Ziegler, T. *Macromolecules* 2002, 35, 7815. (b) D'Amore, M.; Credendino, R.; Budzelaar, P. H. M.; Causá, M.; Busico, V. J. *Catal.* 2012, 286, 103–110.
4. (a) Boero, M.; Parrinello, M.; Terakura, K. *J. Am. Chem. Soc.* 1998, 120, 2746; (b) Boero, M.; Parrinello, M.; Huffer, S.; Weiss, H. J. *Am. Chem. Soc.* 2000, 122, 501; (c) Boero, M.; Parrinello, M.; Weiss, H.; Huffer, S.; *J. Phys. Chem. A* 2001, 105, 5096.
5. D'Amore, M.; Piovano, A.; Vottero, E.; Rudic, S.; Groppo, E.; Bordiga, S.; Civalleri, B. *ACS Appl. Nano Mater.* 2020, 3, 11118-11128.
6. D'Amore, M.\*; Takasao, G.; Chikuma, H.; Wada, T.; Taniike\*, T.; Pascale, F. and Ferrari, A.M.: *J. Phys. Chem. C* 2021, <https://doi.org/10.1021/acs.jpcc.1c05712>.