

Surface Investigation And Nanoscale Morphological Analysis Of Coordinatively Unsaturated Surfaces In Structurally Disordered MgCl_2 And $\text{MgCl}_2/\text{TiCl}_4$ Ziegler-Natta Catalysts

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In this work we propose an innovative approach, which integrates state-of-the-art computational modeling with an experimental strategy having simultaneously a synthetic and a characterization goal. Activated MgCl_2 supports are prepared in situ by controlled de-alcoholation of $\text{MgCl}_2 \cdot 6\text{ROH}$ adduct ($\text{R} = \text{Me}$ or Et), mimicking the routinely adopted methods to synthesize industrial heterogeneous Ziegler-Natta catalysts. The effect of the alcohol in driving the morphology of MgCl_2 crystals, i.e. the type and extension of the exposed surfaces, is investigated. De-alcoholated MgCl_2 is initially characterized in terms of structure and morphology, by means of X-ray Powder Diffraction (XRPD), N_2 physisorption measurements and High-Resolution Transmission Electron Microscopy (HR-TEM).

The experimental data are compared with the results of a systematic computational work conducted with a DFT-D approach and aimed at evaluate the relative stability of the MgCl_2 surfaces both in absence and in presence of the alcohol molecules. According to Bravais' law, the faces that appear on a crystal are parallel to the lattice planes with the larger distance between planes. Hence, an analysis of the $\alpha\text{-MgCl}_2$ planes is performed to locate the most stable surfaces of the crystals and not only the ones of "traditional interest" in catalysis. Papers describing adsorption of donor molecules on MgCl_2 surfaces mostly reported only estimates of enthalpy, since calculation of entropy contributions for surface-adsorbed species is a tedious and time consuming process. However, chemical processes are driven by free energy, and any calculation intended to predict chemical behaviors should produce free energy values. For this reason we underwent an absolutely novel systematic vibrational analysis of crystal families of planes and morphology simulations in order to predict the MgCl_2 crystal shape in presence of alcohol taking into account also the entropic term.

Successively, the surface properties of the de-alcoholated MgCl_2 , and of the corresponding pre-catalyst obtained upon its titration in presence of TiCl_4 vapors, are investigated by means of FT-IR spectroscopy of CO adsorbed at 100 K, which allows to characterize the number and type of exposed surfaces. Assignment of the experimental $\tilde{\nu}(\text{CO})$ data is done by comparison with theoretically computed $\tilde{\nu}(\text{CO})$ values for CO adsorbed on the MgCl_2 model emerging from the morphological analysis. Finally, formation of the active sites upon interaction with triethyl aluminum is investigated by coupling several spectroscopic techniques.

A systematic investigation of all the catalyst's components by means of a multi-technique approach (involving both experimental and theoretical methods) appears to be one of the fundamental step toward understanding their mutual interactions and functions down to a level of detail rarely reached by other methods.