Supporting Information for Publication

Chemisorption-Induced Activation of $MgCl_2$ Film as Realistic Route for Heterogeneous Ziegler-Natta Surfaces under Ultrahigh Vacuum

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Calculation of pyridine adsorption energy

The adsorption energy was calculated based on the numerical details reported in Taniike, T.; Terano, M. Coadsorption and Support-Mediated Interaction of Ti Species with Ethyl Benzoate in $MgCl_2$-Supported Heterogeneous Ziegler-Natta Catalysts Studied by Density Functional Calculations, *Macromol. Rapid Commun.* **2007**, *28*, 1918–1922:

The exchange-correlation functional of Perdew, Burke and Ernzerhof, and the basis set of DNP with effective core potentials were employed within the program of DMOL3. The $MgCl_2$ bulk was assumed to have the α crystalline phase with their lattice constants fixed at the experimental values of 0.3636 and 1.7666 nm. The $MgCl_2$ (110) and (100) surfaces were expressed as a repeated slab, where the vacuum layer of 15A° was taken. The thicknesses of the slabs for the (110) and (100) surfaces were, respectively, set to 6 and 14 atomic layers owing to the balanced performance in accuracy and computational feasibility. For the adsorption of pyridine, a p(2×2) unit cell having 24 $MgCl_2$ was used for the (110) surface and a p(3×1) unit cell having 36 $MgCl_2$ was used for the (100) surface. The 1×1×1 and 2×1×1 *k* points were, respectively, applied to the p(2×2) (110) and p(3×1) (100) surfaces, ensuring the converged adsorption energies. All the atoms were permitted to relax except the bottom two layers of the supports. The convergence criterion for SCF calculations was 1.0×10^{-5} Hartree, and those for the geometry optimization were 2.0×10^{-5} Hartree for energy and 2.1×10^{-3} Hartree/Bohr for the maximum force.

According to the above computational details, the adsorption energy of pyridine was derived as –29.2 and –28.8 kcal/mol on the (110) and (100) surfaces, respectively.