1968
doi:10.1017/S1431927618010322
Microsc. Microanal. 24 (Suppl 1), 2018

Understanding Ziegler-Natta Catalyst Structure via Low-Dose Transmission Electron Microscopy

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Ziegler-Natta catalysts are used to produce a significant fraction of Dow's 16 billion pound annual polyethylene production. The current generation of Ziegler-Natta catalysts is based on titanium active species supported on high surface area magnesium chloride. In spite of the very successful deployment of Ziegler-Natta catalysts in industrial processes, a detailed understanding of the catalyst structure is still lacking. The local morphology and structure of salts such as $MgCl_2$ is poorly explored and rarely reported because imaging the pristine state of these materials at atomic resolution is challenging for two reasons: First, their structural integrity is compromised by any exposure to oxygen or moisture (Figure 1). In addition, such materials are susceptible to damage by the probing electron radiation (Figure 1). Elucidating the atomic-scale structure of $MgCl_2$ materials would lead to beneficial understanding of structure-property relationships of Ziegler-Natta catalysts.

Revisiting the underlying bottlenecks, we take advantage of emerging technologies and new imaging practices. A sealable sample holder is used in combination with low dose-rate in-line holography to simultaneously control air exposure and electron beam damage with remarkable success. The knowledge gained in these studies enriches our basic scientific knowledge about the pristine, atomic structure of previously unexplored matter, and moves science towards capturing functional behavior in the time domain at the atomic resolution.

Under conventional electron imaging conditions at 300 kV, β-phase $MgCl_2$ is observed. This structural determination can be made at accumulated doses of less than 10,000 $e^-/Å^2$ if dose rates around 1500 $e^-/Å^2/s$ are employed. Taking a more careful look at the same $MgCl_2$ material with purposefully controlled electron doses less than 500 $e^-/Å^2/s$, α-phase $MgCl_2$ is detected up to and beyond accumulated doses of ~20,000 e^-/A^2. By systematically increasing the dose rate, a conversion of α-$MgCl_2$ to β-$MgCl_2$ is observed. At significantly higher electron dose rates, chlorine loss is observed as the presence of elemental Mg. The reorganization and damage of the $MgCl_2$-layered structure is induced by both total electron dose and dose rate. By reducing the dose rate on the sample, the total accumulated dose tolerated by the sample can be significantly extended. The damage retardation factor determined by lowering the effective electron dose rate on the $MgCl_2$ sample is a factor of ~ 3 for a dose rate reduction by an order of magnitude.

Atomic-resolution imaging of the pristine α-$MgCl_2$ structure has been achieved by applying low dose rates, a monochromated electron beam, and in-line holography. Thereby, a resolution of 1.7 Å in real space images is demonstrated for alpha and beta $MgCl_2$ structures, which significantly improves on previous literature reports which barely exceeded 5.9 Å (Figure 1), due to the radiation sensitivity of the sample and to microscope limitations.[1-3] Information transfer in the Fourier transform of the real space images reaches close to 1 Å. By limiting the electron dose rate on the sample, we are able to study dislocations in $MgCl_2$ materials. A Fourier-filtered micrograph of pristine α-$MgCl_2$ is shown in Figure 2. Points are highlighted that show terminating $MgCl_2$ lattice planes that occur with a density of ~$7x10^{11}$

cm^{-2}. These defect sites are particularly of interest, as they are thought to be binding sites for the active titanium species for Ziegler-Natta catalysis. Further studies of defect structure and density are currently under way [4].

References:

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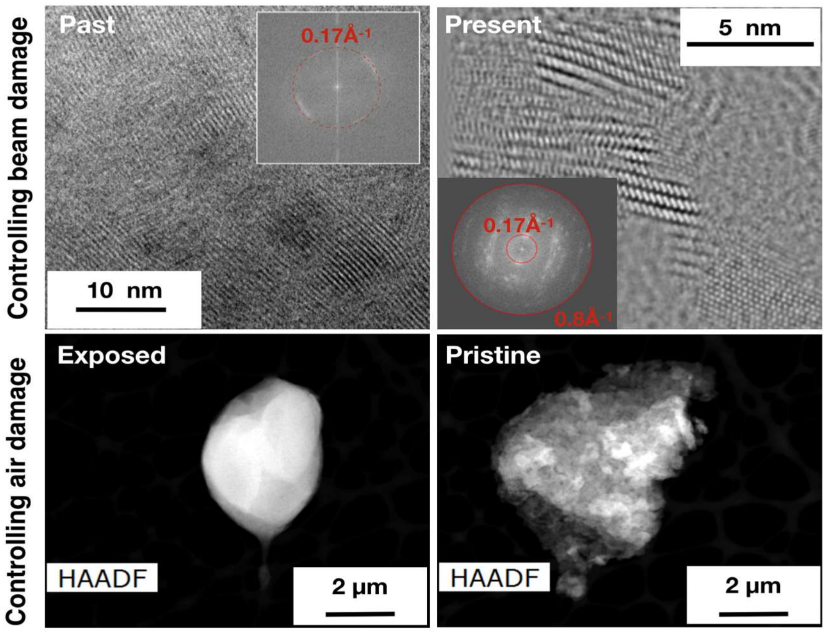

Figure 1. Demonstration of the advancements made in imaging the pristine structure of $MgCl_2$ structures.

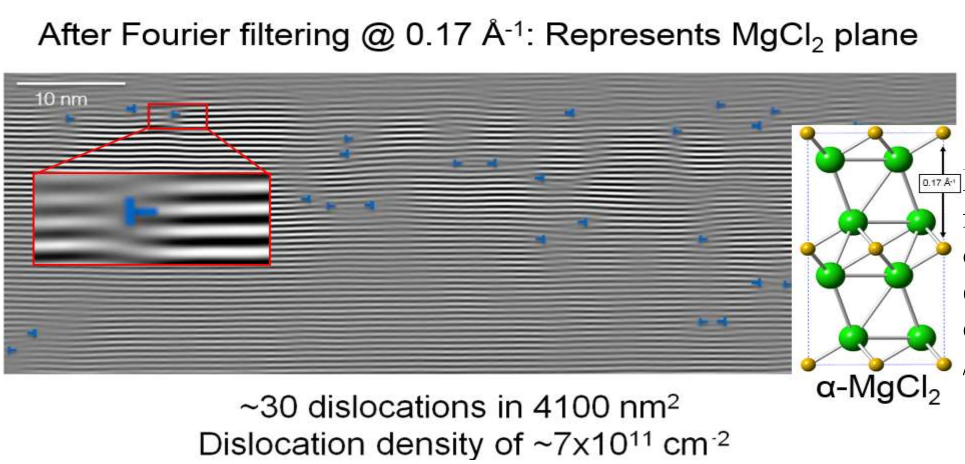

Figure 2. Fourier-filtered micrograph demonstrating defect site density in pristine α-$MgCl_2$ collected with an effective dose rate of ~200 e^-/$Å^2$/s.