MOLTEN SALT SYNTHESIS (MSS) OF MgO(111): CRITICAL FACTORS GOVERNING THE CRYSTALLIZATION PROCESS

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Abstract

In metal oxide catalysis, the performance of the catalyst often depends on the exposed crystal facets. Suitable strategies for controlling the faceting of metal oxide crystals are therefore needed. The generation of high index facets is often desirable given the large number of undercoordinated metal sites that are available for catalytic reactions. Herein we discuss the ability to stabilize these facets during the molten salt synthesis (MSS) of MgO crystals, where the main driving force(s) and factors that determine particle morphology have largely remained elusive. We show that the formation of polar MgO(111) facets is facilitated in salt media when MgO is generated via a liquid-to-solid reaction (with intermediates in the molten state).[1] The presence of residual water and ions impact MgO(111) crystallization in ways that still remain unknown, but are not necessarily governed by adsorption-stabilization processes.

Keywords

Molten salt route, molten salt synthesis, eutectic mixtures, crystallization, magnesium oxide

Introduction

The (photo)catalytic activity of several metals and metal oxides has been found to depend on the crystal facets exposed for a variety of chemical reactions. In general, low-index facets, which in most cases are thermodynamically more stable, show lower activities than high-index facets. Exposed facets with specific ionic spacing(s), as well as particular surface defects (e.g., undercoordinated bonds associated with step and kink sites), can enhance reactivity. The ability to control particle morphology and maximize the exposure of specific crystal planes is of high interest in many applications.

The focus of this study is magnesium oxide (MgO),[1] which has found applications as a catalyst (and catalyst support) for many base-catalyzed organic reactions. Despite significant research in the design and engineering of MgO crystals, simple methods for the controlled preparation of high surface energy MgO facets and studies of facet-dependent properties using this material are scarce.

Xu et al.[2] showed that the decomposition of $Mg(NO_3)_2 \cdot 6H_2O$ in molten $LiNO_3$ results in octahedral MgO particles and hypothesized that strong electrostatic interactions occur between the free ions in the molten medium and the polar (high surface energy) facets of the oxide product. During crystal growth, these interactions presumably lower the surface energies of MgO{111} facets, which results in slower growth rates and a concomitant increase in the relative area of the high-energy facets in the oxide particles. The resulting particles can lead to enhanced catalytic performance. For example, MgO(111) catalysts were shown to be more active than commercial MgO powder in Claisen−Schmidt condensation reactions.[3]

Results and Discussion

We have examined the thermal decomposition of different MgO precursors to assess their influence on the pathways of octahedral MgO particle formation. We found that solid-to-solid conversions and recrystallizations in molten nitrates or chlorides are usually incapable of producing well-defined octahedral MgO, indicating that ion adsorption on MgO (and facet stabilization) may not be the main morphological driving force.
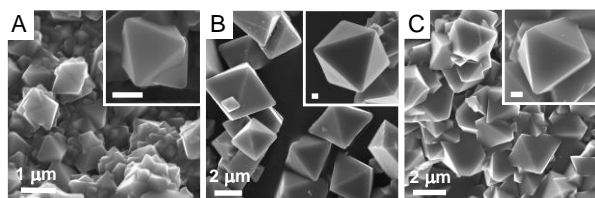

Figure 1. *SEM images of MgO produced by the MSR in (A) LiNO₃, (B) NaNO₃:KNO₃ (1:1), and (C) NaCl:KCl (1:1). All samples were heated to 550 °C for 1 h at 2.5 °C min⁻¹. Inset scale-bars: 400 nm.*

We have shown for $Mg(NO_3)_2 \cdot 6H_2O$, the most suited MgO(111) precursor, that its decomposition trajectory is crucial in determining the exposure of {111} facets. Scanning electron microscopy (SEM) images of MgO produced in $LiNO_3$, $NaNO_3:KNO_3$ and $NaCl:KCl$ media is shown in Figure 1. Complementary characterizations of these materials included TEM/SAED and TGA/DSC.

Scheme 1. *Proposed decomposition pathway in molten nitrate media for $Mg(NO_3)_2 \cdot 6H_2O$. In nitrate-based systems, eutectic mixtures ensure the liquid state of the reaction mixture, favoring a liquid-to-solid mechanism for the formation of MgO.*
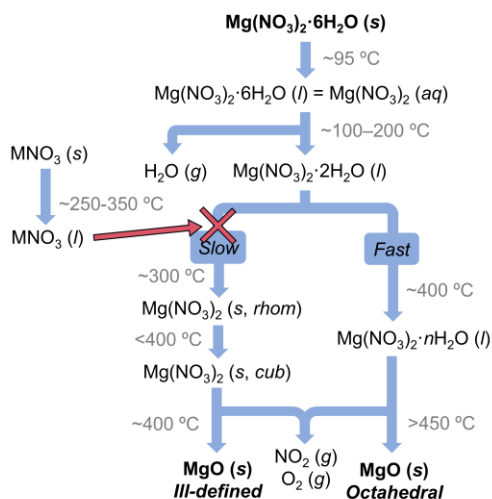
The decomposition trajectory was studied *ex situ* by XRD measurements at intermediate calcination stages. From these measurements we infer that in nitrates the

formation of liquid eutectic mixtures facilitate H_2O retention and ionic mobility, from which well-defined octahedral MgO crystals form (Scheme 1). In a NaCl:KCl medium, MgO(111) crystallization occurs via a molten $K_3NaMgCl_6$ intermediate wherein the H_2O content is negligible (Scheme 2), thus indicating that the presence of water is not the primary driving force.

Scheme 2. *Proposed $Mg(NO_3)_2 \cdot 6H_2O$ thermal decomposition pathway in NaCl:KCl (1:1).*
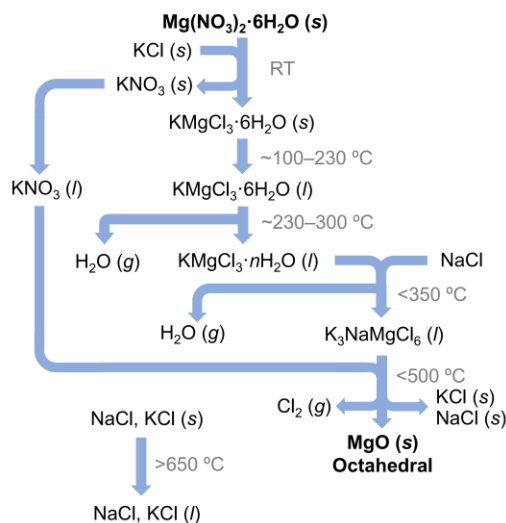
Conclusions

The decomposition of molten intermediates is shown to be critical for the formation of MgO with {111} facets. The observed morphological control cannot be effectively described on the basis of ion adsorption from the molten medium on the forming MgO{111} facets, as previously proposed. Further studies are under way to ascertain the role of the molten intermediates in the oxide crystallization process.

Collectively, our findings underscore the ability to tailor metal oxides with predetermined facets, which opens possibilities to rationally design functional materials with improved properties for catalysis, gas adsorption, and other commercially relevant applications.

Acknowledgments

References

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