

# Towards high-quality manganese oxide catalysts with large surface areas

July 25 2022

## Facile Synthesis of Manganese Oxide Nanoparticles with High Surface Area and Catalytic Activity

Todorokite-type manganese oxides are promising compounds for advanced functional materials

However, it is challenging to achieve both high surface area and catalytic performance

**New one-step method to synthesize todorokite-type manganese oxide octahedral molecular sieve (OMS-1)**

**Starting materials**  
 $Mg(MnO_4)_2$   
 $MnX_2$   
 $MgX_2$   
 $X = OAc^-, NO_3^-$   
 $X_2 = SO_4^{2-}$

pH adjustment

**Low-crystallinity precursor**  
 Buserite

Calcination at 200°C

**OMS-1**

Simple synthesis process

No hydrothermal treatment needed

High surface area and catalytic performance

Durable and reusable

**This solid-state transformation method could enable fine-tuning of manganese oxide nanomaterials to develop efficient catalysts and functional materials**

Synthesis and Aerobic Oxidation Catalysis of Mesoporous Todorokite-type Manganese oxides Nanoparticles by Crystallization of Precursors

Koutani et al. (2022) | *Journal of the American Chemical Society* | DOI: 10.1021/jacs.2c02308

Credit: Tokyo Tech

Manganese oxides have received much attention from materials scientists due to their widespread applications including electrodes, catalysts, sensors, supercapacitors, and biomedicine. Further, manganese is widely abundant and has many oxidation states, which allows it to form various interesting crystalline structures.

One such structure is the "todorokite-type [manganese](#) oxide octahedral molecular sieve (OMS-1)," a crystal whose [unit cells](#) (simplest repeating units of the crystal) consist of three-by-three  $\text{MnO}_6$  octahedral chains. Though promising as a catalyst, the potential of OMS-1 is limited by two reasons. First, its conventional synthesis methods are complex multi-step crystallization processes involving hydrothermal or reflux treatment. Second, these processes tend to create crystals with a higher particle size and a lower surface area, features detrimental to catalytic performance.

In a recent effort to circumvent these problems, a research team from Tokyo Institute of Technology (Tokyo Tech) came up with a simple way to synthesize OMS-1 nanoparticles. Led by Associate Professor Keigo Kamata, the team discovered that the key to easily producing high-quality OMS-1 was to use precursors with low crystallinity. Their study was published in the *Journal of the American Chemical Society*. Additionally, the scientific illustration of this study, created by Dr. Kamata, was selected as a Supplementary Cover Art for the journal.

The researchers called their novel synthesis procedure the "solid-state transformation method." In it, one first needs to combine solutions of  $\text{MnO}_4^-$  and  $\text{Mn}^{2+}$  reagents, such as  $\text{Mg}(\text{MnO}_4)_2$  and  $\text{MnSO}_4$ , at specific ratios. After adjusting the pH of the mixture, one needs to collect the precipitates once they settle. These mainly consist of low-crystallinity

Mg-buserite, a type of layered manganese oxide. The buserite is then calcinated at 200°C for 24 hours, which transforms it into OMS-1 nanoparticles.

Through various experiments performed using advanced equipment, the team thoroughly characterized the OMS-1 they produced. They determined the optimal parameters to obtain the highest yield of the reaction and the best quality OMS-1. A remarkable aspect of the prepared OMS-1 nanoparticles was their surface area, as highlighted by Dr. Kamata: "Our catalyst exhibited a specific surface area of about 250 m<sup>2</sup>/g, which is much larger than that of OMS-1 synthesized using previously reported methods, which only went up to 185 m<sup>2</sup>/g."

To put the synthesized OMS-1 to the test, the researchers investigated its catalytic performance for various alcohol oxidation reactions with oxygen (O<sub>2</sub>) as the only oxidant. The results were highly encouraging. Dr. Kamata comments: "The OMS-1 synthesized through our approach is an effective and reusable heterogeneous catalyst for the oxidation of various types of aromatic alcohols and sulfides. Despite our nanoparticles being ultra-small, they exhibited no trade-off between [surface area](#), particle size, and catalytic performance."

Overall, the findings of this study shed light on how to better control the synthesis of manganese oxide nanoparticles. These insights will hopefully lead not only to highly efficient catalysts but also to novel manganese oxide-based functional materials with practical applications.

**More information:** Maki Koutani et al, Synthesis and Aerobic Oxidation Catalysis of Mesoporous Todorokite-Type Manganese Oxide Nanoparticles by Crystallization of Precursors, *Journal of the American Chemical Society* (2022). [DOI: 10.1021/jacs.2c02308](https://doi.org/10.1021/jacs.2c02308)

Provided by Tokyo Institute of Technology

Citation: Towards high-quality manganese oxide catalysts with large surface areas (2022, July 25)  
retrieved 19 April 2024 from

<https://phys.org/news/2022-07-high-quality-manganese-oxide-catalysts-large.html>

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