



## Short Communication

# A new approach to maintaining the structural integrity of fragile nanostructured heterogeneous catalysts with nanoscale magnetic stir bars

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Three-dimensional (3D) self-assembled nanomaterials with hierarchical architectures are very attractive materials due to their superior physical and chemical properties [1–7]. Over the past few years, a variety of nanomaterials with well-controlled structures were developed and applied in many areas, including water treatment, energy, sensor and catalysis [8–16]. However, robustness and delicacy seem to be exclusive properties for the 3D architectures assembled by nano-sized building blocks. Those delicate structures are usually fragile, and suffer from structural destruction when being exposed to high temperature, strong oxidizing reagents or stress force [17]. Researches have been focused on the rational ways to enhance the structural stability of the hierarchical structures [2,18,19]. Taking the hierarchical flower-like MgO as an example, the O<sup>2-</sup> sites on the surface and hierarchical structures make it a very good heterogeneous base catalyst, but its crisp and fragile structure restrict its utilization in the batch reaction system with forcedly stirring [20]. To keep the 3D flower-like structures, several approaches, including SiO<sub>2</sub> coating [21] and conversion to the hollow spheres [22] were usually adopted. These methods all aimed to enhance the endurance of the catalysts against the stress force from stirring bars.

In this study, we chose another approach. The structural integrity of the fragile catalysts was maintained by using nanoscale stirring bars. The nano stirring bars reduced the strength of the stress force acting on the surface of catalysts. Nanoscale magnetic stir bars are promising materials in several applications [23,24]. Chen's group [23] proposed 1D nanochains assembled by Fe<sub>3</sub>O<sub>4</sub> nanoparticles with great magnetic response, which provided a rudiment for the development of the nanosized stir bars. In our previous work, we utilized the natural magnetotactic bacteria as nanoscale stir

bars in the Pickering emulsion system to enhance the mass transfer in the micro-droplets [25].

Herein, we demonstrated that the structure of fragile flower-like catalyst could be maintained with nanoscale magnetic stir bars. Taking flower-like MgO in the transesterification reaction and Claisen-Schmidt condensation reaction as examples, the flower-like MgO catalyst maintained a remarkable stability with no obvious morphology change and high conversion of the reactants constantly over 5 consecutive runs with nanoscale magnetic stir bars, while the flower-like structure was broken into pieces and the conversion dropped dramatically after only one run with a normal stir bar.

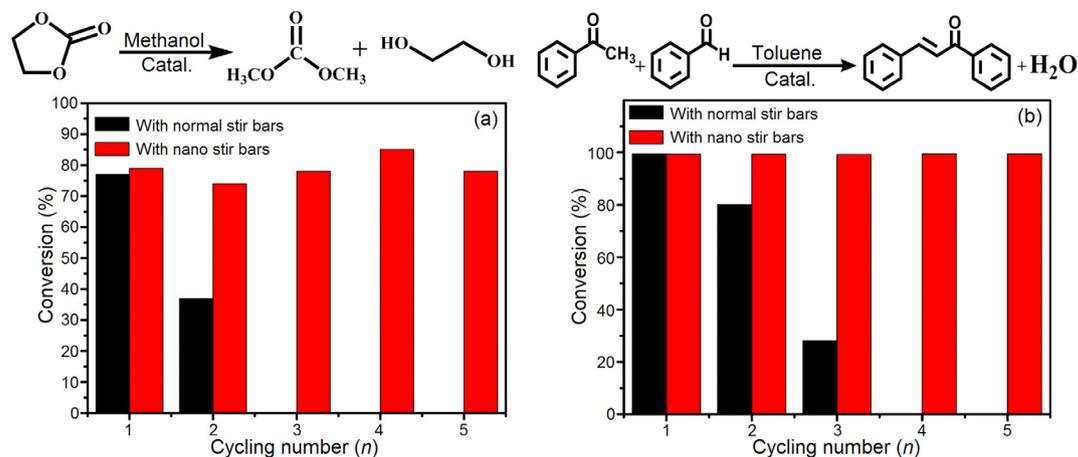
Flower-like MgO catalyst and spindle-shaped yolk/shell Fe@meso-SiO<sub>2</sub> nanoscale magnetic stir bars were prepared according to our previous works, respectively (details can be seen in [Supporting Information](#) and [Figs. S1–S3](#) online). Flower-like MgO was made of pedal-like sub-units, which were further composed of nanoparticles with diameter of 5–6 nm. O<sup>2-</sup> sites on the magnesium oxide are Lewis base sites to catalyze transesterification reaction and Claisen-Schmidt condensation reaction. Moreover, such flower-like hierarchical structures allow the magnesium oxide catalysts to expose more active sites than bulky MgO materials do.

During initial testing of the nanoscale magnetic stir bars under an external magnetic field, the clear supernate became muddy and black instantly when nanoscale magnetic stirring bars began to stir. Then it changed to white after the magnetic field was switched off and nanoscale stir bars were gathered by the magnet ([Fig. S4](#) online). These results confirmed that nanoscale magnetic stir bars could stir the batch reaction system.

To investigate the effect of nanoscale magnetic stir bars on the structure stability of flower-like MgO catalysts, a traditional commercial magnetic stir bar was used under the same condition in the transesterification reaction for synthesis of dimethyl carbonate (DMC). [Fig. 1](#) shows the conversion of ethylene carbonate (EC) in

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**Fig. 1.** (Color online) Stability of MgO for (a) transesterification reaction and (b) Claisen-Schmidt condensation reaction with nanoscale magnetic stir bars and normal magnetic stir bar.

the repeated tests of both systems. In the first run, EC conversion was 79% in the system with nanoscale magnetic stir bars, which was similar to the normal stirring system (77%). However, EC conversion dropped dramatically to 37% in the second run and even dropped to nearly 0% in the rest of cycles with the normal stirring system, while catalysts could still maintain high efficiency with nanoscale magnetic stir bars. Similar results were also observed in the Claisen-Schmidt condensation reaction of benzaldehyde and acetophenone with either a normal stir bar or nanoscale magnetic stir bars (Fig. 1b). After the reaction, the nanoscale magnetic stir bars maintained the similar morphology (Fig. S5 online).

In order to confirm that nanoscale magnetic stir bars were not the actual catalysts in the catalytic reaction, a control experiment without magnesium oxide catalysts under the same condition was performed. The result showed that the reactants had only 0.4% conversion with nanoscale magnetic stir bars (Table S1 online), which proved all active sites were provided by flower-like MgO. In addition, flower-like MgO maintained the crystal phase after re-used in both systems with traditional commercial magnetic stir bar and nanoscale magnetic stir bars.

The maintaining of the hierarchical morphology and high conversion of the reaction could be directly attributed to the replacement of the traditional commercial magnetic stir bar by nanoscale magnetic stir bars. When stirring with traditional commercial magnetic stir bar in the reaction flask, the fragile hierarchical structure of flower-like MgO and the pedals were apt to be broken into pieces. Compared with the origin flower-like MgO, the hierarchical structures were damaged after the first reaction cycle (Fig. 2a, b). The sheet-like fragments of the magnesium oxide were prone to

aggregate and overlap the active sites on the surface, so that the catalytic efficiency dropped sharply and even hard to be collected for the third or fourth run. On the contrary, when stirred by the nanoscale magnetic stir bars, the flower-like MgO structure kept nearly the same as fresh one (Fig. 2c, d). The flower pedals could be seen clearly even after 5 runs.

Generally, force acting on MgO pedals is caused by the agitation of the stirring bars. The strength of the force in a unit area is roughly proportion to the linear velocity of the tip of the stirring bars. Based on the theorem of impulse ( $m \times v = F \times t$ ), a computational simulation of the force strength with normal stir bar and nano stir bar, respectively, were carried out. To simplify the model, mass and time were set as one unit and the rate of the stirring was 500 r/min. As shown in Fig. S6 (online), when the angular velocity is constant, linear velocity follows a linear tendency with the increase of the radius. It means that longer radius of the normal stir bar would provide a much larger force than the random distributed nano stir bars (more than 100-fold) with the same rotation rate. This simulation result further confirms that the strength of the stress force on flower-like MgO is much smaller with nanoscale magnetic stir bars to provide a milder blending, and thus protect the structure stability.

In conclusion, we demonstrated that nanoscale magnetic stir bars could maintain the hierarchical morphology of the fragile catalysts. We envision that this strategy would provide a new approach for the sustainable chemistry and thus a more green and efficient tendency could be developed.

## Conflict of interest

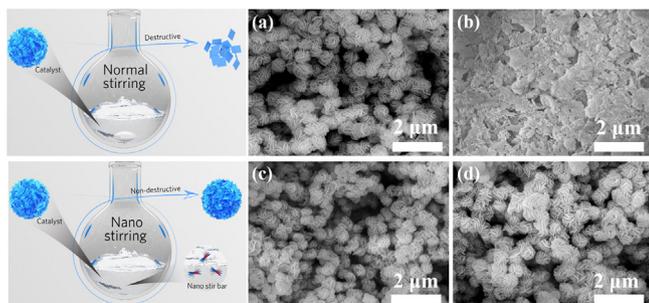
The authors declare that they have no conflict of interest.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scib.2019.01.017>.



**Fig. 2.** (Color online) Scheme illustration of morphology change and corresponding SEM images with (a, b) normal commercial magnetic stir bar and (c, d) nanoscale magnetic stir bars.

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