

STRONG METAL-SUPPORT INTERACTION PROMOTED SCALABLE PRODUCTION OF THERMALLY STABLE SINGLE-ATOM CATALYSTS

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ANNOTATION

Single-atom catalysts (SACs) have demonstrated superior catalytic performance in numerous heterogeneous reactions. However, producing thermally stable SACs, especially in a simple and scalable way, remains a formidable challenge. Here, we report the synthesis of Ru SACs from commercial RuO₂ powders by physical mixing of sub-micron RuO₂ aggregates with a MgAl_{1.2}Fe_{0.8}O₄ spinel. Atomically dispersed Ru is confirmed by aberration-corrected scanning transmission electron microscopy and X-ray absorption spectroscopy.

Keywords: Single-atom, Ru SACs, C-C coupling, fabrication.

INTRODUCTION

In recent years, single-atom catalysts (SACs) have attracted considerable attention as a means by which to maximize precious metal utilization and generate well-defined, uniform active sites. SACs exhibit superior catalytic performance (activity and/or selectivity) for thermal oxidation and hydrogenation⁹, electrochemistry and industrially important processes such as the water-gas shift reaction, C-C coupling, C-H activation, and methanol reforming. Counter-intuitively, SACs were recently reported to exhibit better stability than their nanoparticle (NP) counterparts, highlighting their potential for commercial applications.

Various strategies have been developed for the fabrication of SACs. Atomic layer deposition and mass-selected soft-landing methods offer precise and controllable synthesis of well-designed SACs; however, their scale-up is hindered by high production costs and low catalyst yields. Wet chemical routes, such as incipient wetness impregnation (IWI) and strong electrostatic adsorption methods, are common in laboratory-scale catalyst synthesis. However, they are best suited to low metal loadings and are often time-consuming and process intensive, which is unfavorable for scale-up. In addition, the thermal stability of the resulting SACs is typically poor. Large-scale synthesis of thermally stable SACs therefore remains problematic.

We recently observed that Pt NPs supported on iron oxides can be dispersed into single atoms upon high-temperature calcination. It transpires that a strong CMSI between Fe and Pt is critical to the dispersion process, which also occurs for Fe-doped (but not undoped) Al₂O₃. The chemical similarity of Pt group metals suggests that such interaction may provide a general approach to fabricate thermally stable SACs. Spinels, mixed metal oxides with well-defined structures and excellent thermal stability, are ideal supports for the fabrication of thermally

stable catalysts. The synthesis of a Ru SAC from a Fe-substituted MgAl_2O_4 spinel was therefore explored to verify the generality of this strategy.

A MgAl_2O_4 spinel (designated as MA) and Fe-substituted MgAl_2O_4 spinel ($\text{MgAl}_{1.2}\text{Fe}_{0.8}\text{O}_4$, designated as MAFO) were prepared by solvothermal synthesis and subsequent 700 °C calcination for 5 h as described in the “Methods” section. Supported Ru/MAFO analogs were prepared by conventional IWI of ruthenium(III) acetylacetonate and subsequent calcination at 500 °C (Ru/MAFO-IWI-500) or 900 °C (Ru/MAFO-IWI-900).

X-ray diffraction (XRD) patterns showed that MAFO comprised a pure crystalline spinel phase (Supplementary Fig. 1), indicating that Fe was uniformly incorporated throughout support. The MAFO surface area was far higher than that of commercial Fe_2O_3 (~100 vs. <10 $\text{m}^2 \text{g}^{-1}$, respectively, Supplementary Table 1) offering the prospect of a higher density of anchor sites to immobilize metal atoms. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) revealed small Ru NPs in the uncalcined IWI sample (Supplementary Fig. 2), which disappeared after 900 °C calcination (Supplementary Fig. 3a–c) implying their dispersion into single atoms⁴³. Aberration-corrected (AC) HAADF-STEM images confirmed the formation of uniformly dispersed Ru single atoms (Supplementary Fig. 3d–f). In contrast, lower-temperature (500 °C) calcination resulted in severe sintering of impregnated Ru species into sub-micron RuO_2 aggregates (Supplementary Fig. 4), consistent with our observations for Pt sintering over Fe_2O_3 following low-temperature calcination⁴³. Since the Ru/MAFO-IWI-900 sample transitions through lower temperatures during the heating process, we reasoned that these large RuO_2 aggregates must be thermodynamically unstable and hence should be susceptible to re-dispersion when subject to a further high-temperature calcination. HAADF-STEM confirmed that 900 °C calcination of the Ru/MAFO-IWI-500 sample resulted in complete loss of the RuO_2 aggregates (Supplementary Fig. 5).

The BET surface area of Ru₁/MAFO-900 was 38 $\text{m}^2 \text{g}^{-1}$, hence 1 g of MAFO support provides 38 m^2 of surface (S) after 900 °C calcination. The spinels mainly have primary cuboctahedral shape with dominant {100} and {111} facets⁴⁴. Assuming that all M^{3+} on the surface can stabilize Ru atoms, the theoretical model indicates that the maximum density of atomically dispersed Ru (D) are 5.88 and 6.79 atom nm^{-2} for {100} and {111} facets, respectively. The total number of isolated Ru atoms (N) that could be achieved for 1 g of Ru/MAFO is therefore predicted to be $N = D \times S$. Since the mass of Ru equals $(N/N_A) \times M$, where N_A is Avogadro's constant ($6.02 \times 10^{23} \text{ mol}^{-1}$), and M is the molar mass of Ru (101 g mol^{-1}), the theoretical maximum loadings of isolated Ru atoms that could be dispersed over 1 g of MAFO are 3.7 and 4.3 wt% for {100} and {111} facets, respectively. Thus the calculated maximum Ru loading is about 4 wt% assuming that all M^{3+} sites can stabilize Ru atoms. However, if only Fe^{3+} can stabilize Ru, the maximum Ru loading should be $4 \text{ wt}\% \times 0.8/2 = 1.6 \text{ wt}\%$ for $\text{MgAl}_{1.2}\text{Fe}_{0.8}\text{O}_4$ support. Similarly, the maximum Ru loading should be $4 \text{ wt}\% \times 0.5/2 = 1.0 \text{ wt}\%$ for $\text{MgAl}_{1.5}\text{Fe}_{0.5}\text{O}_4$ support.

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