

Using *Ex-Situ* TEM to Understand Silica-Supported Ruthenium Catalysts

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Due to its nonacidic nature, silica remains a potentially interesting support for catalysis. Unfortunately, silica typically has a weak interaction with metal precursors, and thus, generally results in an inhomogeneous (metal particle clustering) catalyst with low dispersion (large metal particles). Studies, however, suggest that the use of organic precursors can mitigate these issues.¹⁻⁷ Thus, *ex-situ* TEM work was conducted to better understand this phenomenon.

Chemisorption data were collected on three 0.5 wt.% Ru/SiO₂ catalysts (Fig. 1). Each catalyst was prepared by a different synthesis route: (1) an aqueous-based synthesis with no organic precursor, (2) an organic precursor-based synthesis followed by a high temperature calcination step, and (3) an organic precursor-based synthesis followed by a low temperature calcination step. Chemisorption reveals that the aqueous-based synthesis initially results in a highly dispersed catalyst but that this catalyst loses surface area fairly quickly upon thermal treatment under hydrogen. An *ex-situ* TEM study was designed to help explain this behavior. Small, highly clustered Ru particles were found in the aqueous-based preparation (Fig. 2a). The TEM findings are consistent with the aqueous preparation's high initial chemisorption value. A view of the aqueous preparation after a 9 h hydrogen treatment at 400 °C shows the same region of catalyst reveals larger metal particles. This TEM data is consistent with the chemisorption data and suggests relatively easy sintering of the small metal particles due to clustering effects (Fig. 2b).

Chemisorption data also indicates that the organic precursor-based synthesis followed by the high temperature calcination resulted in larger but more stable metal particles (Fig. 1). A TEM analysis of the catalyst, revealed larger, randomly-distributed metal particles on the support surface, a result consistent with the chemisorption finding. Thus, through a combination of chemisorption and TEM studies, it is possible to explain the impact of various synthesis protocols on the development of a thermally stable catalyst with good dispersion.

References:

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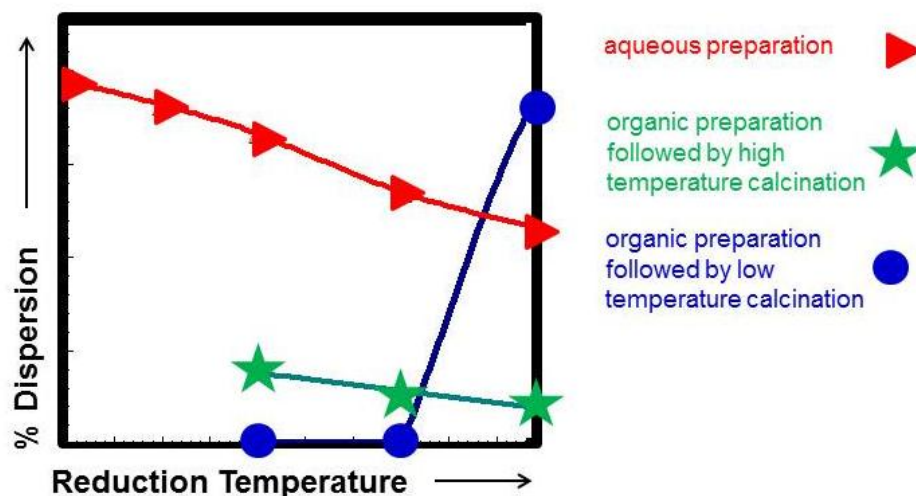


Figure 1: Plot reflects changes in chemisorption value for three thermally treated Ru/SiO₂ catalysts prepared by different synthesis routes. The aqueous preparation results in the highest initial dispersion but a significant decrease in dispersion with thermal treatment. The organic preparation followed by a high temperature calcination presents a lower dispersion but remains relatively stable with thermal treatment. A similar organic preparation followed by a low temperature calcination results in a catalyst having the highest dispersion subsequent to the thermal treatment.

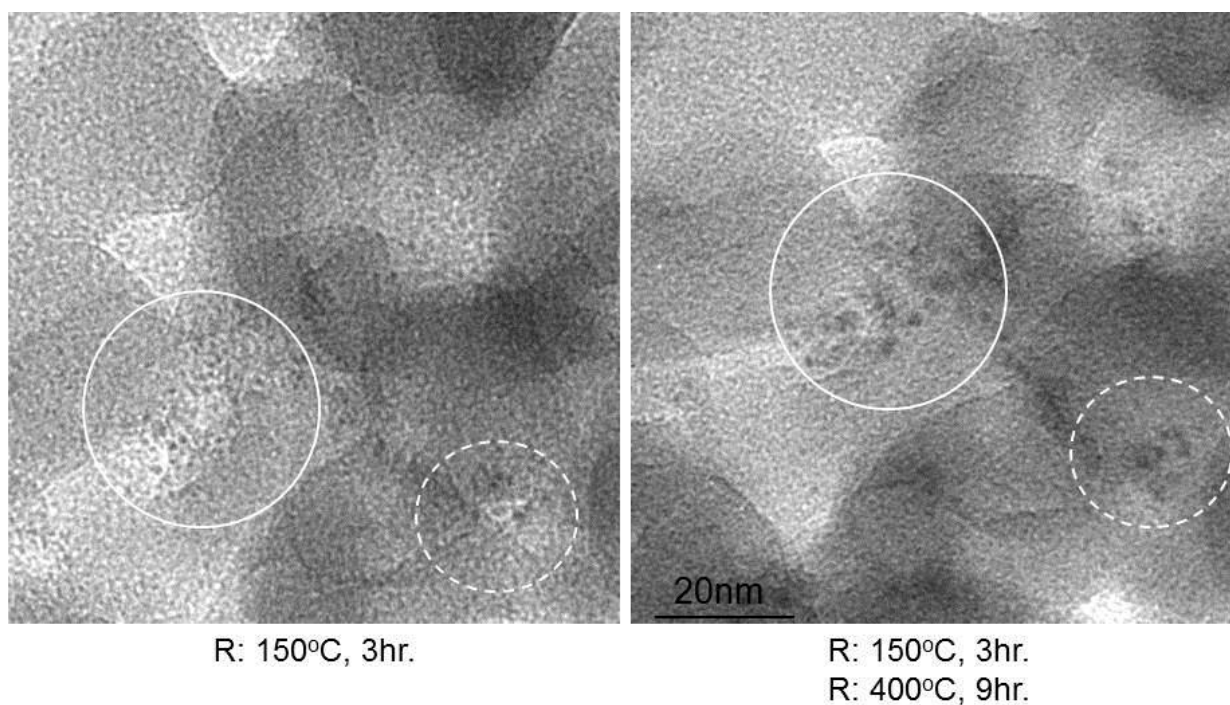


Figure 2: Bright field TEM image presents (a) morphology of Ru/SiO₂ catalyst prepared via aqueous-based synthesis protocol after 150 °C reduction for 3 h and (b) the same area after an additional 400 °C reduction for 9 h. Small metal particle clustering leads to sintering during the thermal treatment and results in the decreased chemisorption value.