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In-Situ TEM / Chemisorption Studies of Alumina-Supported Platinum Catalysts

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Accurate structural and compositional characterization of porous catalytic solids under conditions relevant to their thermal treatment and use remains an important scientific challenge.[1] "Real life" conditions (e.g., temperature, pressure, gas/liquid phase composition, etc.) strongly influence both materials' properties and nanostructure.[1-3] Thus, to better understand these systems, numerous "in-situ" [1-8] and "ex-situ" [9-11] TEM-based protocols have been developed.

In-situ TEM thermal studies provide particularly interesting insights into the low melting point of nanometer-sized metal clusters. Theoretical calculations suggest small particle melting occurs at temperatures well below those for the respective bulk metal.[12-16] In-situ TEM work has confirmed this behavior for ~8 nm Pt particles dispersed on an amorphous carbon film.[17] Our study extends this understanding to an industrially-relevant Pt/Al_2O_3 catalyst. A recent study has suggested that marked differences in catalytic CH_4 activation rates between Pt nanoclusters and bulk single crystals reflect the melting of nanoclusters at typical catalytic reaction temperatures (600-700 ^oC).[18]

Figure 1a presents representative micrographs of neighboring Pt clusters 2-4 nm in diameter on the alumina support. At ambient temperatures, these clusters remain distinct discrete particles separated by ~1 nm. At 400 ^oC (after 1 h in-situ thermal treatment), the two Pt particles start to coalesce (Figure 1b). After additional 1 h thermal treatments at 500 ^oC and 600 ^oC, these coalescence processes were much more evident (Figure 1c and 1d, respectively). These structural observations reveal Pt nanocluster motion at temperatures well below the bulk melting point (~1770 ^oC[19]), suggesting flow and supporting the concept of small metal particle melting point depression. Additional data on isolated Pt particles present a consistent pattern of morphological transformations typical of melting processes. Taken together, these in-situ TEM studies explain chemisorption data that show a consistent decrease in dispersion at constant temperature (500 ^oC) in alumina-supported Pt systems.

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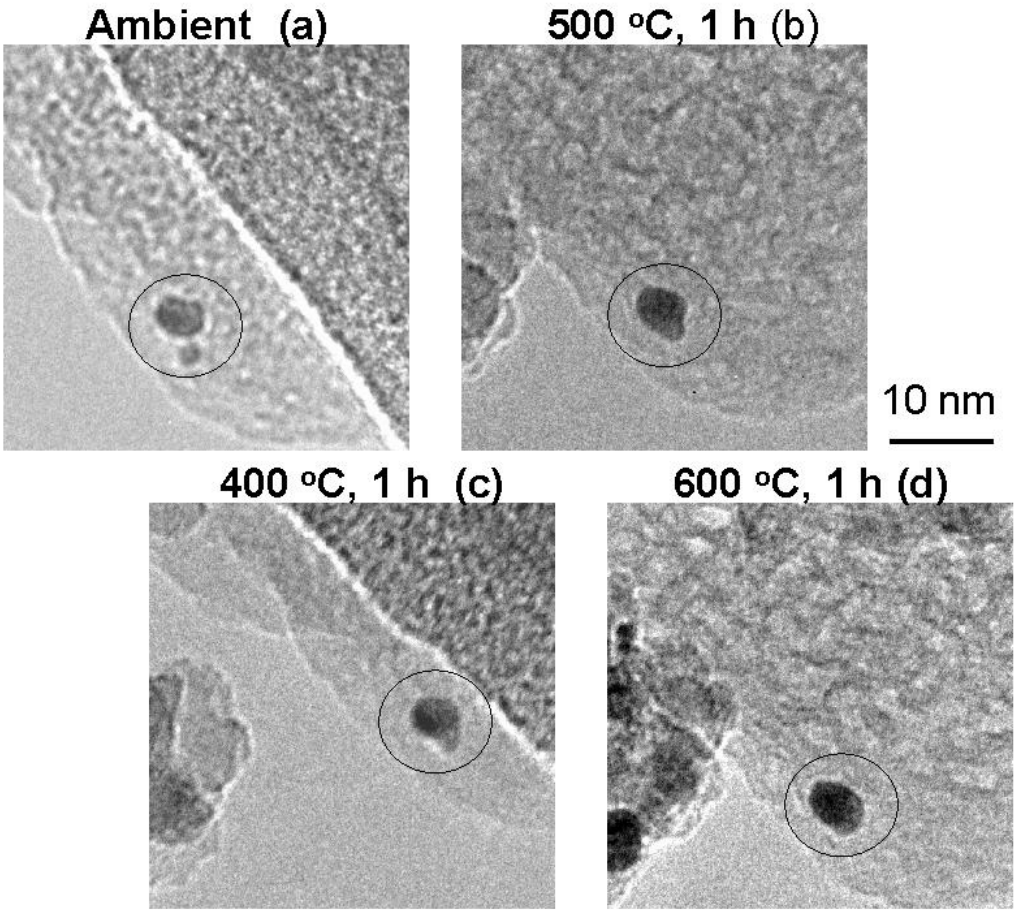

Figure 1: Bright field TEM image showing alumina-supported (a) Pt particles at ambient (~22 °C) temperature and after 1 hour at (b) 400 °C, (c) 500 °C, and (d) 600 °C.

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