

# Early transition metal nanocarbides and nanohydrides by solid-state metathesis initiated at room temperature

Rémi André, Florian D'Accriscio, Guillaume Crochet, Sophie Carenco

Laboratoire de Chimie de la Matière Condensée de Paris, Sorbonne Université-CNRS-Collège de France, 4 Place Jussieu, 75005, Paris, France.

Metal carbides are materials of high interest due to their excellent mechanical resistance (cutting tools) but also for their catalytic activity (Reverse Water Gas Shift reaction, Hydrogen Evolution Reaction, hydrogenation). [1] Their syntheses are commonly performed directly on the metal in presence of carbon at high temperatures (above 1000 °C) which limits their specific surface and therefore their catalytic activity. [2] We recently developed a novel and expeditious way to access finely divided nanoparticles (< 20 nm diameter) dispersed on a hydrophobic carbon support *via* a solid-state reaction, under inert atmosphere, between a metal chloride ( $MCl_x$ ) and metallic potassium dispersed in carbon ( $KC_4$  or  $KC_8$ ) (Figure 1, left). [3] The potassium reduces the metal cation to form KCl and carbide or metallic nanoparticles, the latter being eventually converted into hydrides during the washing step. The high exothermicity of the reaction results in high temperatures, allowing carbide crystallization *in situ*.

Beyond the advantages of this process in terms of green chemistry (no solvent, no heat input and innocuous wastes), the reaction is versatile and was successfully applied to numerous early transition metals (Ti, V, Zr, Nb, Mo, Hf, Ta, W).

In the present work, we studied the impact of different parameters (grain size of precursors, atmosphere, stoichiometry, dispersion of potassium...) on the metal speciation, by Powder X-ray Diffraction (PXRD), and the morphology of the nanoparticles, by Transmission Electron Microscopy (TEM) (Figure 1, right). Playing on the parameters allows the preferential formation of metal carbides ( $Mo_2C$ ,  $W_2C$ , TaC, NbC) or hydrides ( $ZrH_2$ ,  $HfH_{1.7}$ ,  $NbH_{0.8}$ ,  $Ta_2H$ ). We could then propose a general mechanism for the different steps of the reaction (initiation, carburization, hydrogenation) and identify which precursors are the most suitable.

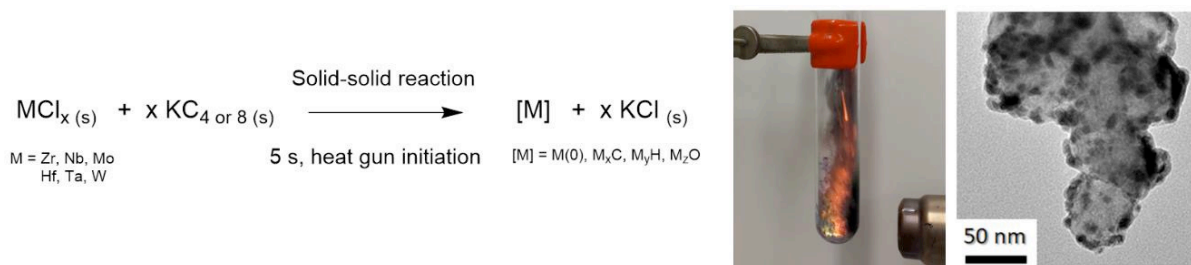


Figure 1: Solid-state synthesis of tungsten carbide nanoparticles on carbon support (left: movie snapshot of the reaction, right: transmission electron micrograph of a tungsten carbide sample)

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