η-Carbides (Co, Mo, or W) Nanoparticles from Octacyanometalates Precursors-Based Network

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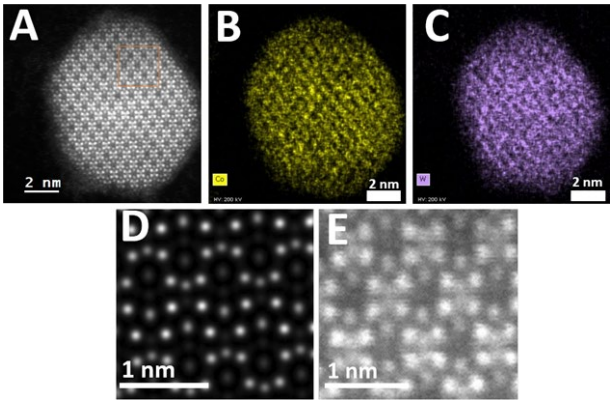
Noble metal nanoparticles such as Au and Pt are well known and widely used for their catalytic properties. Because of the cost of these noble metals, different strategies are pursued to find surrogates to noble metals in catalysis. Emerging and promising approach is to play with NPs of transition metal carbides. Among the candidates for these substitutions are WC NPs [1] ,Mo2C nanoparticles [2] or Co6Mo6C2 combined with graphitic carbon for oxygen reduction. The aim of this study was to develop a route for synthesizing bimetallic carbides NPs in two-step process and the originality of this approach lies in the choice of the metallic precursors.

Octacyanometalate-based networks (OCMs) are 3D metal networks in which the metals are linked together by CN bridges. A water-based surfactant-free synthesis was shown to be applicable for the synthesis of PBAs [3]. It is versatile enough to get networks composed of the combination of any transition metals of our choice. The desired 3D compounds are obtained by mixing a solution of cyanometallates involving one kind of metal (M' = Mo or W) with a solution of another metallic salt of the second metal (M = Co). To turn the metalate network into metallic carbide, the OCMs undergo heat treatment, under inert atmosphere as the procedure used by Aparicio et al [4].

In bimetallic particles, different types of η-carbides-type structures were evidenced in our sample. Co3Mo3C, Co6Mo6C, and Co2Mo4C from the Co-Mo-C system. Co3W3C (fig 1), Co6W6C, Co4W2C, and Co2W4C from the CO-W-C system. These compounds were identified by combination of Transmission Electron Microscopy, high resolution STEM/HAADF imaging of individual NPs (fig A), EDS analysis (fig B-C), and compared simulated (fig D) and experimental HAADF-STEM image (fig E). The size of these carbide nanoparticles is 5 nm in average. Along with η-carbides, the presence of monometallic carbide nanoparticles such as Mo2C and WC has also been observed. The pyrolysis temperature is an important factor in the formation of nanoparticles. Indeed, a treatment at a too low temperature, < 700 °C for Co-Mo system and 800 °C for Co-W system will not enable the complete transformation of the precursors. Beyond these temperatures, η-carbide nanoparticles account for the majority of the nanoparticles observed (> 60%).

Co3M'3C, Co6M'6C, Co2M'4C (M' = Mo or W), and Co4W2C, metallic carbide nanoparticles were successfully synthesized by thermal decomposition of Cs-Co-M' precursor octacyanometalate networks. Their presence in significant proportions in a definite temperature range attests for the efficiency of the synthesis route by thermal decomposition of OCM. The strength of this method also lies in the wide choice of metals that can be used to fabricate octacyanometalate-based networks and thus potentially the wide choice of carbides nanoparticles that could be made easily and rapidly accessible

Graphic:



Keywords:

eta-carbides, STEM/HAADF, catalysts

Reference:

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