

Nanostructured Catalytic and Magnetic Materials: Sonochemical Synthesis and Characterization

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Final Seminar

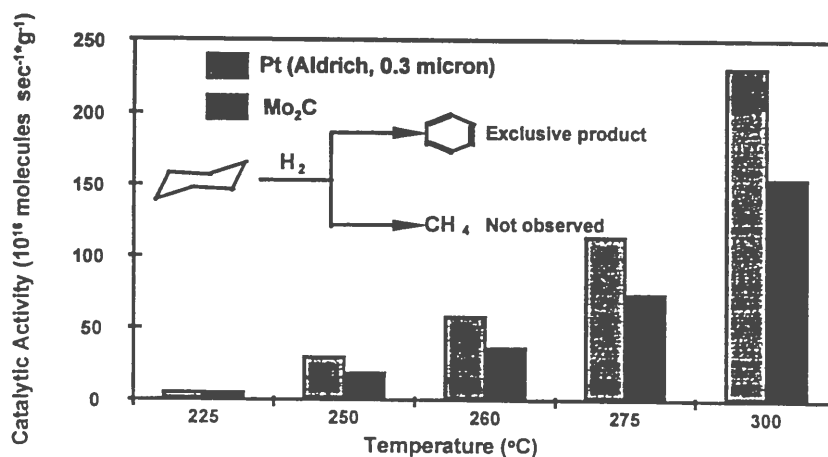
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Sonochemistry arises from acoustic cavitation; the formation, growth, and implosive collapse of bubbles in a liquid. The implosive collapse of bubbles generates localized hot spots; temperature of ~5000 K and pressure of ~1800 atm, with a cooling rates that exceed 10^{10} K/s [1-3]. Using these extreme conditions, we have developed a new synthetic technique for the synthesis of nanostructured materials. When solutions of volatile organometallic precursors are irradiated with high intensity ultrasound, particles consisting of nanometer size clusters are formed. Various classes of nanostructured materials including metal powders, metal colloids, and supported heterogeneous catalysts have been generated simply by changing the reaction medium [4-6].



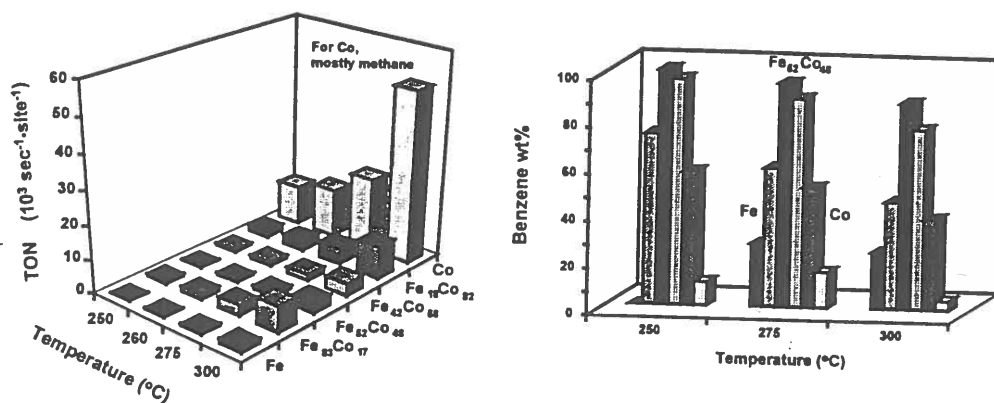
Sonochemical decomposition of molybdenum hexacarbonyl produced nanostructured metal carbide. After thermal treatment, pure molybdenum carbide without oxygen or carbon contamination was produced. The material consists of highly porous aggregates of 2-3 nm sized particles with a very high total surface area ($>130 \text{ m}^2/\text{g}$) [7]. These carbides are excellent dehydrogenation catalysts with selectivity and activity comparable to Pt [8]. Sonochemically prepared molybdenum carbide is an active catalyst for Fischer-Tropsch synthesis with an activity comparable to that of the conventional supported iron catalysts.

	After synthesis	After thermal treatment
Composition	$\text{Mo}_2\text{C}_{1.9}\text{O}_{1.45}$	$\text{Mo}_2\text{C}_{0.97}$
Surface area	$188 \text{ m}^2/\text{g}$	$130 \text{ m}^2/\text{g}$
Particle size	2 nm	3 nm

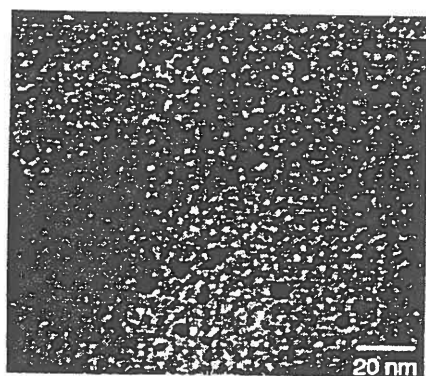


Nanostructured metals (Fe and Co) and alloys (Fe-Co) have been synthesized by sonochemical decomposition of volatile organometallic precursors ($\text{Fe}(\text{CO})_5$ and

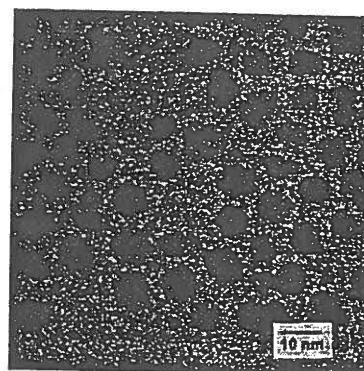
$\text{Co}(\text{CO})_3(\text{NO})$) [9]. The sonochemically prepared Fe, Co, and Fe-Co alloys have large surface areas relative to bulk metal even after heat treatment. The sonochemically prepared Fe, Co, and Fe-Co powders have high catalytic activity for the dehydrogenation and hydrogenolysis of cyclo-hexane. Compared to conventionally prepared Fe-Co alloys, the sonochemically prepared Fe-Co alloys have much higher catalytic selectivities for the dehydrogenation of cyclohexane to benzene, with 1:1 ratio Fe-Co alloys having selectivities as high as 100% [10]. The carbonaceous deposit on the surfaces of sonochemically prepared catalysts is at least one of the reasons causing the higher dehydrogenation selectivity. The sonochemically produced cobalt has a porous structure and high surface area. It is an active catalyst for Fischer-Tropsch synthesis and its high surface area leads to greater activity than that exhibited by commercial cobalt powder.



Nanometer iron and cobalt particles dispersed in a polyvinylpyrrolidone (PVP) matrix have been synthesized by sonochemical decomposition of $\text{Fe}(\text{CO})_5$ and $\text{Co}(\text{CO})_3(\text{NO})$. Transmission electron micrographs show that these particles range in size from 3 to 8 nm. Electron microdiffraction revealed that the particles are amorphous, and after *in situ* crystallization these particles become bcc iron and fcc Co.



Fe/PVP in hexanol



Fe/Oleic acid in hexadecane

Magnetic measurements revealed that these nanometer iron particles are superparamagnetic with a saturation magnetization of 100 emu/g at 290K [11]. Cobalt colloid stabilized by PVP is weakly paramagnetic but after refluxing it becomes an extremely soft ferromagnet with a saturation magnetization of 160 emu/g. Particle growth and extensive catenation are responsible for the changes in its magnetic properties.

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