

Nanostructured Molybdenum Carbide: Sonochemical Synthesis and Catalytic Properties

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The preparation of nanophase materials has been the focus of intense study in materials science.^{1,2} A variety of chemical and physical preparative methods have been applied to produce materials with nanometer structure, including metal evaporation,³ decomposition of organometallic compounds,⁴ and reduction of metal salts.^{5,6} Sonochemical decomposition of transition metal carbonyl compounds has also been proven to be a useful technique to generate nanophase transition metals.^{7,8}

Recently, molybdenum and tungsten carbides have been examined as heterogeneous catalysts because their activity is often similar to that of the platinum group metals.^{9–11} For catalytic applications, high surface area materials are generally needed; the preparation of interstitial carbides of molybdenum and tungsten with high surface areas, however, is very difficult. We present here a simple sonochemical synthesis of nanostructured molybdenum carbide from the ultrasonic irradiation of molybdenum hexacarbonyl. In addition, we have examined the catalytic activity and selectivity of these materials for the dehydrogenation of alkanes.

The chemical effects of ultrasound arise from acoustic cavitation: the formation, growth, and implosive collapse of bubbles in a liquid.^{12,13} The collapse of bubbles generates localized hot spots through adiabatic compression or shock wave formation within the gas of the collapsing bubble. This local heating produces a wide range of high-energy chemistry. The conditions formed in these hot spots have been experimentally determined, with transient temperatures of ~5000 K, pressures of ~1800 atm, and cooling rates in excess of 10¹⁰ K/s.^{14,15} Using these extreme conditions, we have explored a variety of applications of ultrasound to materials chemistry.¹⁶

A slurry of molybdenum hexacarbonyl (1 g in 50 mL of hexadecane) was sonicated with a high-intensity ultrasonic horn (Sonic and Materials, model VC-600, 0.5 in Ti horn, 20 kHz, 100 W cm⁻²) at 90 °C for 3 h under argon to yield a black

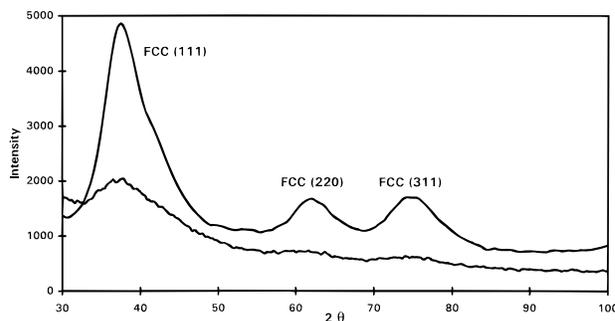


Figure 1. X-ray powder diffraction patterns of sonochemically produced Mo₂C. The lower curve is immediately after sonolysis; the upper curve is after heat treatment at 450 °C under He.

powder. The powder was filtered inside an inert atmosphere box (Vacuum Atmospheres, <1 ppm O₂), washed several times with purified, degassed pentane, and heated at 100 °C under vacuum. X-ray powder diffraction¹⁷ (XRD) showed extremely broad peaks centered at a *d* spacing of 2.4, 1.5, and 1.3 Å (Figure 1), which did not match body-centered cubic (bcc) lines of molybdenum metal. After the heat treatment at 450 °C under helium flow for 12 h, sharper peaks in the XRD were observed at *d* spacing values of 2.39, 1.49, and 1.27 Å which accurately correspond to face-centered cubic (fcc) molybdenum carbide, Mo₂C (Figure 1). The synthesis of Mo₂C is particularly prone to substantial oxygen contamination.⁹ Even after heat treatment at 450 °C under helium, oxygen was still present at about 4 wt %. Since the presence of oxygen could poison the catalytic activity, it was removed prior to catalytic studies by heating in a flowing 1:1 CH₄/H₂ mixture at 300 °C for 1 h, then at 400 °C for 1 h, and finally at 500 °C for 48 h. The flow rate of the CH₄/H₂ mixture was 27.5 cm³ (STP)/min. After this carburization, excess carbon, hydrogen, and oxygen had been largely removed. The elemental analysis results showed the sample was very pure (theoretical for Mo₂C, 94.11 % Mo, 5.89 % C; exptl., 93.86 % Mo, 5.68 % C, 0.08 % H, 0.06 % N), which corresponds to a stoichiometry of Mo₂C_{0.97}. The XRD was essentially unchanged by carburization.

The scanning electron micrographs showed that the surface is extremely porous. Before carburization, high-resolution transmission electron microscopy revealed that the material is a porous aggregate of 2 nm sized particles (Figure 2). The particle diameter calculated from the line broadening of X-ray powder diffraction was 1.6 nm.¹⁸ Surface area, determined by BET gas adsorption isotherms, was found to be 188 m²/g. After carburization, the material remains a porous aggregate with particle size increasing slightly to 3 nm in diameter; the BET surface area decreased slightly to 130 m²/g.

The catalytic activity and selectivity of the sonochemically produced molybdenum carbide were examined for the dehydrogenation versus hydrogenolysis of cyclohexane with a flow catalytic microreactor.¹⁷ This reaction was chosen because the suppression of hydrocarbon cracking during dehydrogenation

(17) X-ray powder diffraction data were collected on a Rigaku D-max diffractometer using Cu Kα radiation ($\lambda = 1.5418$ Å). Scanning electron micrographs were taken on a Hitachi S800 electron microscope, and transmission electron micrographs were taken on a Phillips CM-12 electron microscope. All characterizations were accomplished without exposure of samples to air. Catalytic studies were done in a quartz reactor with a flow of hydrogen at 27.5 cm³ (STP)/min to carry the cyclohexane vapor at a constant partial pressure of 0.1 bar, and products were analyzed with a quadrupole mass spectrometer (Spectra Instruments) and gas chromatograph (Hewlett-Packard 5730A) on an *n*-octane/Porasil C column with flame ionization detector. Total conversions were kept to roughly 10% to minimize complications due to heat and mass transfer and to secondary reactions of the products.

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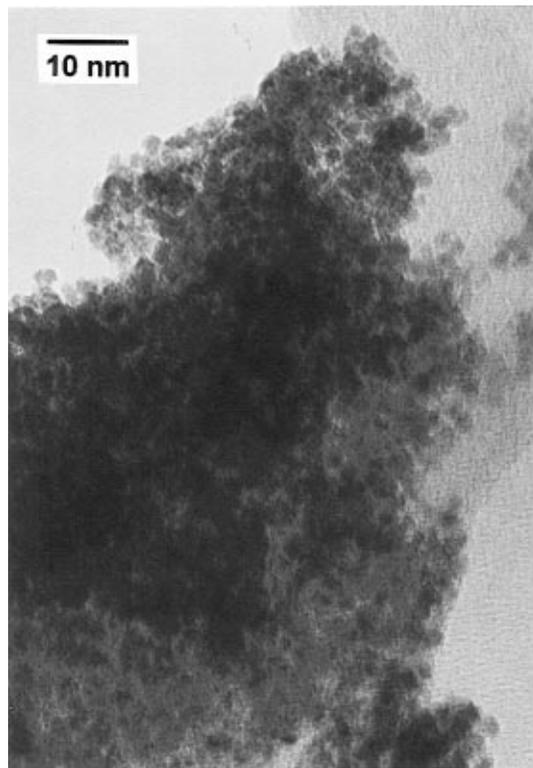


Figure 2. Transmission electron micrographs of sonochemically produced Mo₂C.

remains an important challenge for non-platinum catalysts.^{19,20}

To compare the catalytic properties, commercial ultrafine powders of platinum and ruthenium (Aldrich Chemicals Co., 0.27–0.47 μm diameter) were also used under identical conditions, after heating at 400 °C for 3 h under H₂ flow to remove surface contaminants. Figure 3 shows the catalytic activity (in terms of turnover frequency of cyclohexane molecules converted per second per gram of catalyst) as a function of temperature

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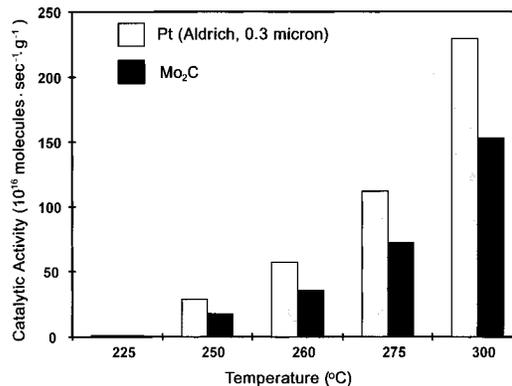


Figure 3. Catalytic activity for dehydrogenation of cyclohexane of a sonochemically produced Mo₂C sample after carburization under CH₄/H₂ and commercial ultrafine platinum powder after heating under H₂.

for the Mo₂C sample pretreated under CH₄/H₂ at 500 °C for 48 h compared to commercial ultrafine platinum powder.

At all reaction temperatures examined, benzene was the *only* product formed for both samples and their activities were comparable; no hydrogenolysis products were detected. In contrast, only hydrogenolysis, mostly to methane, occurred with commercial ruthenium powder. The analogy has often been made that Mo₂C is similar to Ru whereas W₂C behaves like Pt.⁹ These results demonstrate, however, that for dehydrogenation of alkanes, sonochemically prepared nanostructured molybdenum carbide has a selectivity similar to that of Pt rather than to that of Ru.

In conclusion, sonochemical decomposition of molybdenum hexacarbonyl produces nanometer-sized powders of face-centered cubic molybdenum carbide. The material consists of highly porous aggregates of 2 nm sized particles with very a high total surface area. Mo₂C generated sonochemically is an excellent dehydrogenation catalyst with selectivity and activity comparable to those of Pt.

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