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Sonochemical Preparation of a Nanostructured Bifunctional Catalyst

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The catalytic conversion of methane to higher hydrocarbons, in particular aromatics such as benzene, is extremely important for the effective utilization of natural gas. This transformation has been performed with bifunctional catalysts, most notably metal-impregnated zeolite ZSM-5.[1−7] Lunsford and co-workers[8] have carefully studied the kinetics of Mo on ZSM-5, which becomes an active catalyst for dehydroaromatization, and concluded that the active phase is actually Mo_2C. Various methods of preparation such as incipient wetness and ion exchange, however, produce nonuniform materials that have varying catalytic activity and selectivity. We have previously developed a sonochemical preparation of nanostructured, high surface area Mo_2C.[9] While this form of Mo_2C is a very active dehydrogenation catalyst for cyclohexane,[9] it shows no activity for methane aromatization. We report here a simple sonochemical preparation of a bifunctional "eggshell" catalyst for the conversion of methane to benzene. Because the Mo_2C clusters are formed during acoustic cavitation inside a collapsing bubble, their deposition on the ZSM-5 occurs only on the outer surface of the zeolite, and thus does not obstruct the channels of the ZSM-5 support.

Sonochemical preparation of nanophase materials arises from acoustic cavitation: the formation, growth, and implosive collapse of bubbles in a liquid irradiated with high-intensity ultrasound.[10] During the collapse of such bubbles, local hot spots are created with controllable temperatures as high as ∼5000 K,[11] which provides an unusual method for the decomposition of volatile organometallic precursors. Of particular relevance for supported catalysts, the event responsible for the formation of metal clusters is the gas phase of the collapsing bubble, which is therefore separate from the oxide support onto which the clusters attach.[12] This *inherently* generates "eggshell catalysts" where the outer surface of the support holds the nanometer sized catalyst particles. Given the surface accessibility of such catalysts, they often exhibit enhanced activity compared to conventionally prepared analogs.[10]

In the preparation of Mo_2C/ZSM-5, $Mo(CO)_6$ and HZSM-5 were irradiated as a slurry in hexadecane with ultrasound at 20 kHz for 3 h at 85 °C under Ar flow.[13] Scanning transmission electron microscopy (STEM)[14] shows that the channel structure in the zeolite corresponding to the (200) and (020) faces was maintained for both the control of sonicated HZSM-5 and the sonochemically prepared Mo_2C/ZSM-5. These lattice fringes separated by 10 Å (quantified by Fourier diffractography) are shown in Figure 1a. The dark field image of the Mo_2C/ZSM-5 shows uniform particles of about 2 nm in diameter dispersed uniformly on the outer surface of the ZSM-5 support (Figure 1b). EDX detection was used to quantify local elemental concentrations of the Mo_2C/ZSM-5 by high-resolution spot analysis using a 1 nm beam width (which is on the order of the Mo_2C particle size). Multiple Mo_2C particles (shown as lighter areas in Figure 1b) were analyzed and compared to particle-free areas on the ZSM-5 support. Spot EDX analyses of adsorbed Mo_2C particles gave a high Mo/Si molar ratio (as high as 0.8), whereas analyses of regions without Mo_2C particles showed essentially no detectable Mo (Mo/Si ratios are 0.04 ± 0.02). For comparison to our sonochemically prepared catalyst, we synthesized Mo_2C/ZSM-5 by the conventional incipient wetness method,[8] impregnating ZSM-5 with $(NH_4)_6Mo_7O_{24}$, and examined its microstructure by STEM-EDX. The distribution of Mo_2C particles onto ZSM-5 was *much* more uniform in the sonochemically prepared samples.[15]

X-ray photoelectron spectroscopy (XPS) analysis,[16] which has a depth penetration of ∼50 Å, confirms that the Mo_2C is concentrated on the surface of the ZSM-5 support. The electronic states of the Mo, C, and support were also analyzed by XPS. The Mo_2C is characterized by a spin-coupled doublet for the $Mo(3d_{5/2})$ and $Mo(3d_{3/2})$ peaks and the C(1s) peak at characteristic binding energies.[16b] Analysis of the Mo(3d) and Si(2p) peak intensities gave a Mo/Si mole ratio of 0.15, while the bulk elemental analysis gave a Mo/Si mole ratio of 0.01. This comparison means that there is more than a 15-fold enhancement of surface Mo versus the bulk material.

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(12) At 20 kHz, the cavitation bubble will be on the order of 100 μm in size, and much too large to occur within the nm pores of a zeolite.

(13) $Mo(CO)_6$ (0.053 g) and HZSM-5 (1.0 g, Si/Al = 50, $H_{1.88}$-$(Al_{1.88}Si_{94.18}O_{192})$) (Zeolyst Intl., Kansas City, KS) were added to dry hexadecane (35 mL) in an Ar-filled glovebox (Vacuum Atmospheres, <0.5 ppm O_2). The reaction slurry was irradiated with high-intensity ultrasound at 20 kHz and ∼80 W/cm² with a 1 cm² titanium horn (Sonics & Materials VCX600) for 3 h at 85 °C under Ar flow. After sonication, the reaction vessel was brought into the glovebox and the mixture was filtered, washed with degassed, dry pentane (60 mL), and then heated for 5 h under vacuum at 80 °C to remove any unreacted $Mo(CO)_6$. Excess carbon contamination was mostly removed by treating the catalyst at 450 °C for 10 h under 1:1 CH_4/H_2 (30 cm³/min) flow; typical samples were prepared at 2 wt % Mo. As a control, another HZSM-5 sample was sonicated as described without the addition of $Mo(CO)_6$ and given identical posttreatment and compared to the above material.

(14) Scanning transmission electron microscopy (STEM) utilized a VG HB501 microscope with EDX detection (Oxford Instruments). Long exposure to the electron beam must be avoided for zeolite samples to avoid sample degradation during STEM. (b) Reimer, L. *Transmission Electron Microscopy*, 2nd ed.; Springer-Verlag: Berlin, 1989; pp 452−457.

(15) The conventionally made sample had a wide distribution of Mo_2C particle sizes on the ZSM-5 support, ranging from greater than ≈20 nm down to ≈2 nm. In addition, not all ZSM-5 particles had uniform amounts of Mo_2C on their surfaces. Furthermore, there were also substantial numbers of free Mo_2C particles not in contact with ZSM-5 particles. In comparison, the sonochemically synthesized material has a homogeneous distribution of Mo_2C particles (≈2 nm) all supported on uniformly coated particles of ZSM-5.

(16) (a) X-ray photoelectron spectroscopy was recorded on a Phi-540 Perkin-Elmer spectrometer using Mg Kα radiation. The XPS was internally calibrated to the known Si (2p) peak at 102.9 eV in ZSM-5; Briggs, D. *Practical Surface Analysis*, 2nd ed.; John Wiley & Sons: Chichester, 1990; Vol. 1, pp 407−413. (b) For sonochemically prepared Mo_2C, the $Mo(3d_{5/2})$ and $Mo(3d_{3/2})$ peaks are at 228.6 and 231.7 eV, internally calibrated to the background C(1s) peak at 283.5 eV: Moulder J. F.; Stickle, W. F.; Sobol, P. E.; Bomben, K. D. *Handbook of X-ray Photoelectron Spectroscopy*; Chastain J., Ed.; Perkin-Elmer: Eden Prairie, MN, 1992. (c) XPS analysis of both the O(1s) and Si(2p) in the HZSM-5 and the HZSM-5 control sample gave an O/Si atomic ratio of 2.1, as expected.

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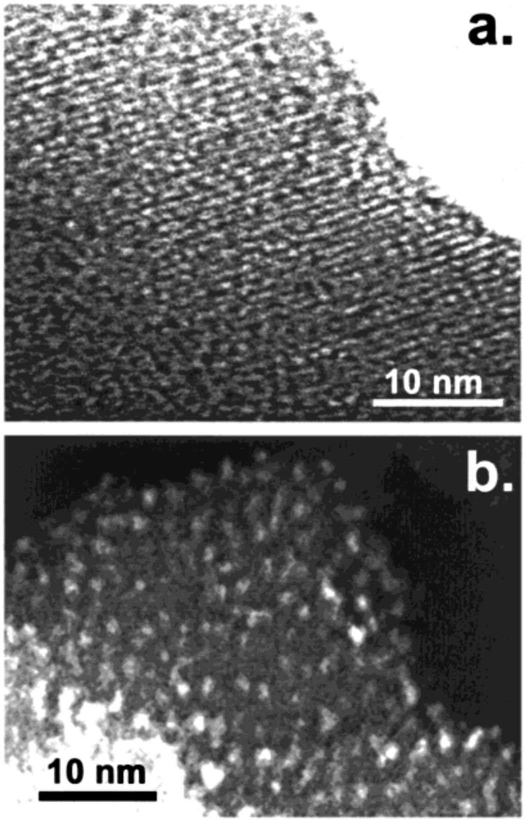

Figure 1. STEM micrographs of Mo_2C/ZSM-5 prepared sonochemically showing (a) the lattice fringes of the ZSM-5 and (b) a typical dark field image showing Mo_2C particles on the surface of the ZSM-5.

To assess the dispersion of Mo_2C on the ZSM-5 support (i.e., the fraction of surface atoms of $Mo_{(carbidic)}$), chemisorption with CO was done at room temperature. The catalyst was pretreated by heating it to 400 °C for 3 h under high vacuum (10^{-5} Torr) to remove any adsorbed gases. The chemisorption isotherms gave a dispersion of 34% CO-binding surface metal sites per total metal in the sample. An approximation of particle size for the Mo_2C/ZSM-5 catalyst was modeled after that used for Pt/SiO_2 catalysts (eq 1).[17,18]

$$d_{\text{particle}} = 1.105(d_{\text{atomic}})(N_t)^{1/3} \tag{1}$$

where N_t is the total number of $Mo_{(carbidic)}$ atoms per particle for a dispersion of 34%. This equation assumes the particles are cubooctahedral with $d_{\text{atomic}} = 0.29$ nm (the inter-Mo distance for Mo_2C) and a 1:1 binding stoichiometry for CO:$Mo_{(carbidic)}$.[19] For 34% dispersion, $N_t \sim 1700$ and the particle diameter is ~3.8 nm. This value is somewhat larger than the 2 nm particle diameter directly observed by STEM, probably due both to the surface Mo atoms in direct contact with the zeolite (which are unavailable for CO chemisorption) and to partial carbon coating of the Mo_2C surfaces.

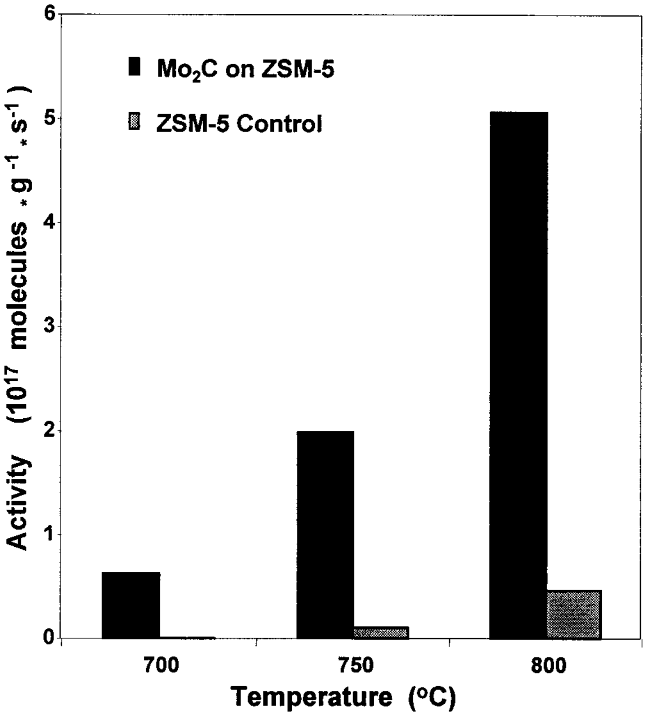

Figure 2. Catalytic activity for dehydroaromatization of methane by sonochemically prepared Mo_2C/ZSM-5 and sonicated ZSM-5 control.

Catalytic studies on the Mo_2C/ZSM-5 powder for the dehydroaromatization of methane to benzene were performed with a single-pass quartz microreactor[20] at 700 to 800 °C. The observed turnover frequencies based on CH_4 consumption are shown as a function of temperature in Figure 2 and compared to the sonicated ZSM-5 control. The product distribution is comprised of ethane and benzene, with selectivity for the latter of 60% at 700 °C. The sonicated HZSM-5 control sample treated in the same way does not show any significant activity. Literature values for other Mo_2C/ZSM-5 catalysts are reported as approximately 6×10^{17} molecules g^{-1} s^{-1} at 700 °C with a 70% selectivity for benzene,[8] quite comparable to the sonochemically prepared samples.

In conclusion, the sonication of molybdenum hexacarbonyl in hexadecane with HZSM-5 has been shown to produce nanophase Mo_2C particles of about 2 nm decorating the outside of the ZSM-5 support. This eggshell catalyst has essentially all of the Mo_2C on the outer surface of the ZSM-5 support relative to the pores. The catalyst is both active and selective for the aromatization of methane to benzene.

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(20) Ultrahigh purity (99.99%) CH_4 was used with a flow of 12 cm^3/min. The reaction products were analyzed with a quadrupole mass spectrometer (Spectral Instruments) and gas chromatograph (Hewlett-Packard) with an *n*-octane/Porasil C column and FID.