

ULTRASOUND MEDIATED SYNTHESIS OF CATALYTIC AND POLYMERIC MATERIALS

Gennady Dantsin

Final Seminar

May 8, 2001

Sonochemical preparation of nanophasic materials arises from acoustic cavitation: the formation, growth, and implosive collapse of bubbles in a liquid irradiated with high-intensity ultrasound. The implosive collapse of these bubbles generates localized hot spots within the bubbles with temperatures up to 5000 K, pressures of at least 400 atm, and cooling rates on the order of 10^{10} K/s.^{1,2} These high energy conditions are utilized for the synthesis of nanostructured materials when the liquid contains volatile precursors.³ In addition, ultrasonic emulsification of strong reductants can be used to mediate the polymerization of a class of inorganic and organic polymers, called polycarbynes.

This research is divided into two parts. The first part describes the ultrasonic synthesis, characterization, and catalytic applications of a nanostructured bifunctional aromatization catalyst. Such materials have applications in the conversion of natural gas to more industrially useful liquid fuels such as benzene. The second part of this research involves the design, polymerization, and attempted conversion of carbon-based network polymeric precursors to diamond-like films. The pyrolysis and stabilization of such films by chemical vapor deposition technology is explored.

Nanostructured Molybdenum Carbide Supported on HZSM-5

Nanostructured Mo_2C has previously been sonochemically synthesized in our laboratory.⁴ This material consisted of highly porous aggregates of 2-3 nm particles with very high surface areas. Sonochemical decomposition of molybdenum hexacarbonyl in a hexadecane solution in the presence of HZSM-5 generates a $\text{Mo}_2\text{C}/\text{ZSM-5}$ bifunctional catalyst.⁵ This material consists of a HZSM-5 support with Mo_2C particles, 2-3 nm in diameter, homogeneously dispersed on the outer surface of the zeolite, thus creating an “eggshell” catalyst (Figure 1).

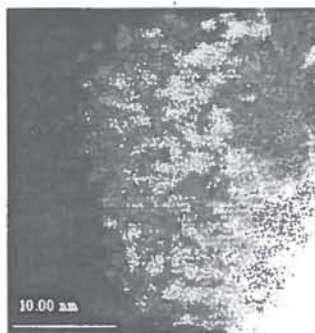


Figure 1. Dark field electron micrograph of sonochemical $\text{Mo}_2\text{C}/\text{ZSM-5}$.

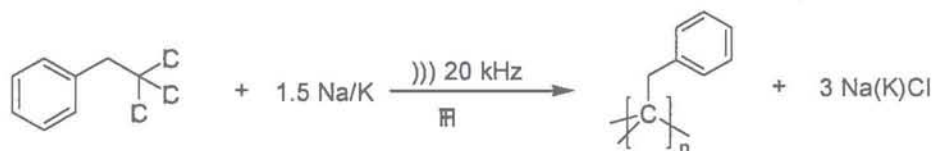
Characterization of the surface composition by XPS and comparison to bulk elemental composition confirms a 15-fold enhancement of Mo₂C concentration on the surface of the catalyst support HZSM-5. Electron microscopy and CO chemisorption measurements were used to characterize the dispersion of Mo₂C particles; 34% of the total Mo in the sample is able to chemisorb CO.

In contrast to conventionally prepared Mo/ZSM-5, the sonochemically prepared catalyst requires no induction period but rather is immediately active.^{6,7} The selectivity and activity of the sonochemically prepared catalyst is comparable to its conventionally prepared counterpart.

Polymer to Diamond-like Carbon

The goal of this research was to develop a polymeric precursor for CVD diamond deposition in order to overcome the high substrate temperature (~1000°C) currently needed in diamond film formation. Previous attempts in diamond particle formation from poly(phenylcarbyne) will be discussed^{8,9} and a more rational polymer design is proposed. The synthesis and pyrolytic activity of the new polymer is discussed, as is its reaction chemistry under CVD conditions.

The organic monomer was designed such that it would yield a network polymer whose weakest bond is between the sp³ hybridized all carbon backbone and the capping unit (benzyl group). Synthesis of the monomer, 2,2,2-trichloroethylbenzene, by a Meerwein arylation and subsequent polymerization by a Wurtz-type reductive coupling with ultrasonically emulsified Na-K alloy generated poly(benzylcarbyne).



GPC and laser light scattering experiments revealed that the polymer does indeed have a network type structure rather than a linear one. The maximum MW obtained by light scattering was ~14 kDa. Characterization of the polymer structure was carried out by solution and solid state NMR and is consistent with a quaternary backbone carbon bonded to a benzyl group.

The thermal decomposition profile for this polymer was established by TGA-MS.(Figure 2) As expected the benzyl-carbon bond was preferentially broken, but no diamond film was formed. The carbon backbone was then stabilized under hot filament chemical vapor deposition conditions, in which atomic hydrogen typically stabilizes the growing diamond film. The advantage of this methodology is a lower deposition temperature: ~400 °C versus 1000 °C for conventional CVD formation with methane, however no diamond was observed. Poly(benzylcarbyne) was also used as a chemical nucleation layer for conventional hot filament CVD deposition under 1%CH₄/H₂ flow. The relatively low molecular weight of the polymer (~140-mer) was insufficient to

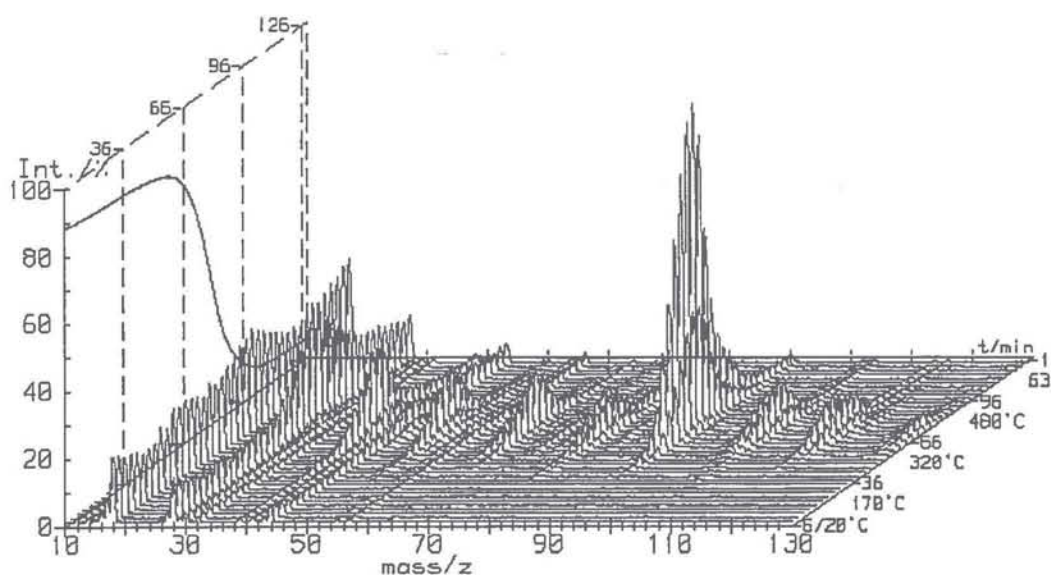


Figure 2. Thermogravimetric analysis with MS of poly(benzylcarbyne).

overcome the diffusion requirement at the substrate of the CVD reactor. A high molecular weight poly(benzylcarbyne) following the same methodology developed here might lead to a low temperature route to CVD diamond film formation.

References

1. Flint, E. B.; Suslick, K. S. *Science* **1991**, *253*, 1397.
2. McNamara, W. B., III; Didenko, Y.; Suslick, K. S. *Nature* **1999**, *401*.
3. Suslick, K. S.; Fang, M. M.; Hyeon, T.; Mdeleleni, M. M. *NATO ASI Ser., Ser. C* **1999**, *524*, 291-320.
4. Hyeon, T.; Fang, M.; Suslick, K. S. *J. Am. Chem. Soc.* **1996**, *118*, 5492-5493.
5. Dantsin, G.; Suslick, K. S. *J. Am. Chem. Soc.* **2000**, *122*, 5214-5215.
6. Wang, L.; Tao, L.; Xie, M.; Xu, G.; Huang, J.; Xu, Y. *Catal. Lett.* **1993**, *21*, 35-41.
7. Wang, D.; Lunsford, J. H.; Rosynek, M. P. *J. Catal.* **1997**, *169*, 347-358.
8. Visscher, G. T.; Nesting, D. C.; Badding, J. V.; Bianconi, P. A. *Science* **1993**, *260*, 1496-9.
9. Bacsa, W. S. *Science* **1994**, *266*, 1256-57.