

## Sonochemical Synthesis of Nanophase Metals, Alloys and Carbides

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### ABSTRACT

Sonochemistry arises from acoustic cavitation; the formation, growth, and implosive collapse of bubbles in a liquid. The implosive collapse of bubble generates localized hot spot; temperature of  $\sim 5000$  K and pressure of  $\sim 1800$  atm, with heating and cooling rates that exceed  $10^7$  K/s. Using these extreme conditions, we have developed a new synthetic technique for the synthesis of amorphous and nanostructured inorganic materials. When irradiated with high intensity ultrasound in low volatility solvents under argon, volatile organometallic precursors produce high surface area, amorphous solids that consist of agglomerates of nanometer clusters. For Fe and Co, nanostructured metals and alloys are formed that are non-crystalline by x-ray, neutron, and e-beam diffraction. For Mo and W, metal semicarbides, e.g.,  $\text{Mo}_2\text{C}$  are produced. These nanostructured solids are active heterogeneous catalysts for hydrocarbon reforming and CO hydrogenation. Using polymeric ligands (e.g., polyvinylpyrrolidone) or oxide supports (alumina or silica), the initially formed nanoscale clusters can be trapped as colloids or supported catalysts.

### INTRODUCTION AND BACKGROUND

Study of the chemical effects of mechanical actions go back to the turn of the century, when Ostwald's definition of "mechanochemistry" set the foundation for its systematic study. The field of tribochemistry, as developed by Thiessen, Heinicke, Kubo, and Avvakumov, among others [1], helped reveal an enormous diversity of chemical reactions that occur during solid surface-surface interactions [2-3]. Our own work on the chemical effects of ultrasound in liquids and liquid-solid systems has addressed similar phenomena induced by various mechanical processes that ultrasound can create, including acoustic cavitation, turbulent flow, microjet formation, and shock waves [4-5].

The chemical effects of ultrasound are diverse and have applications in the fields of synthetic organic, inorganic, materials, and polymer chemistry, for both stoichiometric and catalytic reactions [6-9]. In some cases, ultrasonic irradiation can increase reactivity by nearly a

million-fold [11]. The chemical effects of ultrasound fall into three areas: homogeneous sonochemistry of liquids, heterogeneous sonochemistry of liquid-liquid or liquid-solid systems, and sonocatalysis (which overlaps the first two). Because cavitation cannot occur in solids, chemical effects are not generally observed during ultrasonic irradiation of solids or solid-gas systems.

The primary physical event responsible for sonochemistry is acoustic cavitation: the formation, growth, and implosive collapse of bubbles in a liquid. The implosive collapse of bubbles generates localized hot spots, with transient temperatures of  $\sim 5000$  K, pressures of  $\sim 1800$  atm, cooling rates in excess of  $10^{10}$  K/s [12-14].

Using these extreme conditions, we have explored a variety of applications of ultrasound to materials chemistry, including the development of a new synthetic technique for the synthesis of nanostructured inorganic materials. When solutions of volatile organometallic compounds are irradiated with high intensity ultrasound, high surface area solids are produced that consist of agglomerates of nanometer clusters [15-18]. As discussed here, nanostructured metals and alloys are formed from Fe and Co precursors, whereas for Mo and W, the metal carbides (e.g.,  $\text{Mo}_2\text{C}$ ) are produced. These sonochemically produced nanostructured solids are active heterogeneous catalysts for hydrocarbon reforming and CO hydrogenation. Using polymeric ligands (e.g., polyvinylpyrrolidone) or oxide supports (alumina or silica), the initially formed nanoscale clusters can be trapped as colloids or supported catalysts, respectively.

These sonochemical preparations fit well with recent interest in nanostructured materials and catalysts [19-21]. While there are a variety of chemical and physical preparative methods to produce such materials (e.g., metal atom evaporation, thermal decomposition of organometallic compounds, and the reduction of metal salts), this remains a challenging goal for transition metal materials and new synthetic techniques are needed.

## EXPERIMENTAL DETAILS

All manipulations for the preparation of samples were performed using Schlenk vacuum line and inert atmosphere box (Vacuum Atmospheres,  $< 1$  ppm  $\text{O}_2$ ) techniques. Pentane was distilled over sodium/benzophenone. Decane and hexadecane were distilled over sodium. Ultrasonic irradiation was accomplished with a high intensity ultrasonic probe (Sonic and Materials, model VC-600, 1 cm diameter Ti horn, 20 kHz,  $100 \text{ W cm}^{-2}$ ).

X-ray powder diffraction data were collected on a Rigaku D-max diffractometer using  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). Scanning electron micrographs were taken on a Hitachi S800 electron microscope. Transmission electron micrographs were taken on a Phillips CM-12 electron microscope. Samples for elemental analysis were submitted in sealed vials without exposure to air.

Hydrogen (99.99%, Linde), methane (99.97%, Matheson) and CO (99.0+%, Linde) were further purified through 4A molecular sieves and oxy-traps (Alltech). Cyclohexane (99+%, Fisher) was dried over molecular sieves prior to use. In cyclohexane reaction, a MKS mass flow controller maintained the flow of hydrogen at  $27.5 \text{ cm}^3$  (STP)/min to carry the cyclohexane vapor at a constant partial pressure of 0.1 bar through the catalyst. A quartz reactor was used for both adsorption and gas-solid catalytic studies. The catalysts were transferred from an inert atmosphere box to the catalytic rig without exposure to air. Surface areas were calculated by applying the BET equation to the  $\text{N}_2$  adsorption isotherm measured at 77 K. The gas products obtained during the temperature-programmed desorption (TPD) and temperature-programmed

reaction (TPR) experiments were analyzed by a quadruple mass spectrometer (Spectra Instruments). The catalytic reaction products were analyzed by gas chromatography (Hewlett-Packard 5730A) on a n-octane/Porasil C column with flame ionization detector.

For the preparation of nanostructured Fe/SiO<sub>2</sub> catalysts, silica gel (Universal Scientific Incorporated chemicals, 63-100 mesh) was pretreated at 450°C under vacuum (1×10<sup>-5</sup> Torr) for 10 hours before use. To this, a solution of Fe(CO)<sub>5</sub> in dry decane was added, and the slurry was irradiated at 20°C with a high-intensity ultrasonic probe for 3 hours under argon. After irradiation, the black powder was filtered and washed with dry pentane in an inert atmosphere box.

Conventional silica-supported crystalline iron catalysts were prepared using the incipient wetness impregnation method by dissolving Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O in an aqueous solution containing silica gel. These samples were dried at 220°C for 12 hours, and calcined at 450°C under an O<sub>2</sub> flow for 1 hour. Reduction of iron supported on silica was carried out in a flow of hydrogen at 200°C for 1 hour, at 300°C for 1 hour, and finally at 450°C for two hours.

The synthesis of nanostructured Fe-Co alloy catalysts followed a procedure similar to that developed for the sonochemical synthesis of amorphous iron [15-18]. Solutions containing various relative concentrations of Fe(CO)<sub>5</sub> and Co(CO)<sub>3</sub>(NO) were irradiated in dry decane at 0°C with a high-intensity ultrasonic probe for 3 hours under argon. After irradiation, black powders were formed, which were filtered and washed with dry pentane in the glove box.

Nanostructured molybdenum carbide catalyst were prepared by ultrasonic irradiation of a slurry of molybdenum hexacarbonyl in hexadecane was sonicated at 90°C for 3 hours under argon. Hexadecane was chosen as a solvent because its vapor pressure is low at the sonication temperature. The black powder was filtered inside a dry box, washed several times with purified, degassed pentane.

## RESULTS AND DISCUSSION

There is an inherent versatility to our sonochemical synthesis of nanostructured metals, alloys, and metal carbides: various forms of nanophase materials can be generated simply by changing the reaction medium (Scheme 1). When Fe, Co, or Ni precursors are sonicated in high boiling alkanes, nanostructured metal powders are formed. By ultrasonic irradiation in the presence of a polymeric ligand (e.g. polyvinylpyrrolidone (PVP)), stable nanophase metal colloids can be isolated and characterized. A transmission electron micrograph of the nanocolloid Fe/PVP is shown in Figure 1. Additionally, sonication of the precursor in the presence of an inorganic support (silica or alumina) provides an alternative means of trapping the nanometer clusters formed during cavitation and produces active supported heterogeneous catalysts.

Because the primary reaction site of sonochemistry is the gas phase inside a cavitating bubble, volatile precursors are required [13]. Good thermal stability is also important, so that decomposition takes place only during cavitation. Metal carbonyls and nitrosyls are particularly well suited to these requirements. In addition, the solvent vapor pressure should be low at the sonication temperature, because significant solvent vapor inside the bubble reduces bubble collapse efficiency [5].

Scheme 1. Sonochemical synthesis of various forms of nanostructured materials.

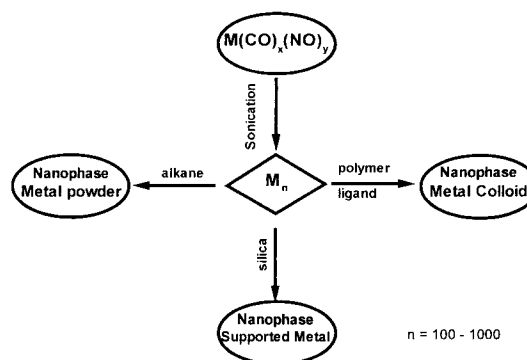
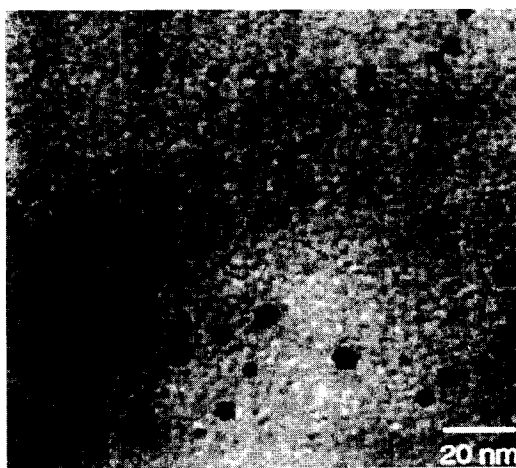


Figure 1. Transmission electron micrograph of nanostructured Fe colloid sonochemically prepared in polyvinylpyrrolidone, obtained on a Phillips 420 electron microscope.



### Nanostructured Silica-Supported Fe

Ultrasonic irradiation of decane solutions of iron pentacarbonyl ( $\text{Fe}(\text{CO})_5$ ) in the presence of silica gel produces a silica-supported amorphous nanostructured iron. The iron loading on the  $\text{SiO}_2$  can be easily varied by changing the initial concentration of the  $\text{Fe}(\text{CO})_5$  solution. Elemental analysis reveals Fe, Si, O and a trace amount of carbon (<1%) to be present. The origin of carbon most likely arises from the decomposition of CO or the alkane solvent during ultrasonic irradiation.

The amorphous nature of these supported iron particles has been confirmed by several different techniques, including differential scanning calorimetry (DSC), X-ray powder diffraction, and electron-beam microdiffraction. Differential scanning calorimetry shows one irreversible exothermic transition at  $335^\circ\text{C}$  corresponding to a disorder-order transition (i.e., crystallization) of the amorphous iron. X-ray powder diffraction shows no diffraction peaks from the material as initially prepared; after heat treatment under He at  $400^\circ\text{C}$  for 4 hours, which is sufficient to induce

crystallization, only the lines characteristic of  $\alpha$ -Fe metal (d spacings of 2.03, 1.43, 1.17 and 1.04 Å) are observed. After crystallization, the X-ray powder diffraction pattern contains no peaks attributable to iron oxide, iron carbide or other iron-based phases. Electron microdiffraction with a transmission electron microscope confirms these observations and shows only a diffuse ring characteristic of amorphous iron particles.

The transmission electron micrograph showed that the iron particles produced by sonolysis of  $\text{Fe}(\text{CO})_5$  were highly dispersed on the  $\text{SiO}_2$  surface. The iron particles range in size from 3 to 8 nm. Chemisorption of CO permits measurement of the dispersion and the average particle size of iron supported on silica surfaces [22]. CO chemisorption measurement data at  $-78^\circ\text{C}$  on our samples gives an average iron particle size of 7 nm, in good agreement with the TEM data.

The catalytic activity of the silica supported nanostructured iron was probed in the commercially important Fischer-Tropsch synthesis reaction (i.e., hydrogenation of CO). The catalytic activity (in terms of turnover frequency of CO molecules converted per catalytic site per second) of silica-supported nanophase iron and conventional silica-supported iron (prepared by the incipient wetness method) were compared as a function of temperature, for samples with a high iron loading and low dispersion (to minimize the effects of support and dispersion). The sonochemically produced iron on silica catalyst is an order of magnitude more active than the conventional supported iron. Moreover, the silica-supported nanostructured iron catalyst exhibits high activity at low temperatures ( $<250^\circ\text{C}$ ), whereas the silica supported conventional iron catalyst has no activity. We suggest that the dramatic difference in activity between the two samples below  $300^\circ\text{C}$  may be due to the amorphous nature of iron and the inherently highly-defected surface formed during sonolysis of  $\text{Fe}(\text{CO})_5$ , when the amorphous state of iron is preserved. At higher temperatures, activity decreases, which may be due to iron crystallization, surface annealing, or catalyst deactivation from surface carbon deposition.

### Nanostructured Fe-Co alloys

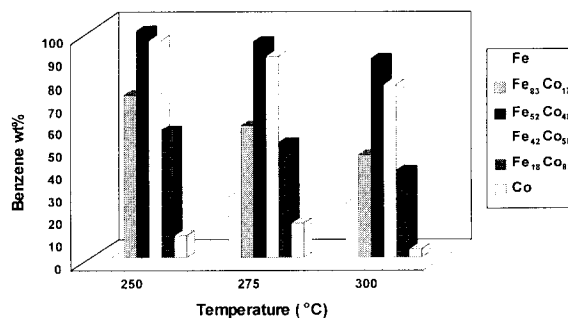
$\text{Fe}(\text{CO})_5$  and  $\text{Co}(\text{CO})_3(\text{NO})$  were chosen as precursors because of their high vapor pressures at modest bulk solution temperatures where they are still thermally stable. The composition of the Fe-Co alloys can be controlled simply by changing the ratio of solution concentrations of the precursors; alloy compositions ranging from pure Fe to pure Co are readily obtained.

The solid-solution nature of the alloys was confirmed by TEM-EDX results, which were made on different spots of the polycrystalline alloy powders. The EDX results show that the alloys are homogeneous on a nanometer scale. The original Fe, Co, and Fe-Co alloys produced by ultrasound are amorphous, as determined by XRD, electron-beam microdiffraction, and DSC, but do contain  $\approx 1$  wt. % C as initially prepared. After heat treatment under  $\text{H}_2$  gas flow at  $400^\circ\text{C}$  for 2 hours, all samples underwent crystallization. The XRD results show no peaks attributable to iron/cobalt oxide, iron/cobalt carbide or other iron/cobalt impurity phases. Pure Fe crystallizes to cubic (bcc) structure, pure Co crystallizes to cubic (fcc) and hexagonal (hcp) mixed structures. All the alloys that we have tested so far crystallize in the bcc structure; this is consistent with the known Fe-Co equilibrium phase diagram that strongly favors the bcc structure [23]. Elemental analysis results show that nearly pure metal and alloys are produced after  $\text{H}_2$  treatment (in the best cases, 99.9% metal and  $<0.1\%$  C, H, N). SEM at high magnification indicates that these materials are porous aggregates of small clusters of 10-20 nm

particles. Surface electronic structures and surface compositions of the sonochemically prepared Fe-Co alloys were also examined by using x-ray photoelectron spectroscopy (XPS). The XPS measurements have been performed on heat treated samples before catalytic reactions. The electronic structures of the surfaces of these samples appear to be the same as the pure metals. The surface compositions of the alloys demonstrate some small enrichment of Fe over Co. Similar trends towards an iron-enriched surface have been reported by other researchers with other preparations using coprecipitation methods [24].

Catalytic studies of the sonochemically prepared Fe-Co alloys were made for cyclohexane dehydrogenation and hydrogenolysis reactions. All catalysts were treated under H<sub>2</sub> gas flow at 400°C for 2 hours before the catalytic studies. While this does not alter the nanostructure of the material significantly, it does cause crystallization of the nanometer clusters. H<sub>2</sub> treatment is necessary, however, to provide a reproducible catalytic surface. Two kinds of products were formed during the cyclohexane reaction: benzene was the only dehydrogenation reaction product and aliphatic hydrocarbons (mostly methane) were the hydrogenolysis reaction products. The catalytic selectivity (in terms of the percentage of benzene among all the reaction products) as a function of temperature is shown in Figure 2. The catalytic properties of the sonochemically prepared Fe, Co and Fe-Co alloys in the cyclohexane reaction exhibit interesting trends. First, they are all active catalysts for cyclohexane conversion: pure Co has the highest activity (albeit primarily for hydrogenolysis), pure Fe has the lowest activity, and Fe-Co alloys have intermediate activity between pure Fe and pure Co. Second, Fe-Co alloys generate much more dehydrogenation product (benzene) than pure Fe or Co. Third, the 1:1 Fe/Co alloy has both much higher dehydrogenation activities and selectivities at all reaction temperatures (250°C to 300°C) than the other alloys or pure metals. In the best cases, the selectivity for dehydrogenation approaches 100%.

Figure 2. The selectivity of Fe, Co, and Fe-Co alloys for catalytic dehydrogenation versus hydrogenolysis of cyclohexane as a function of temperature.



### Nanostructured molybdenum carbide

Molybdenum and tungsten carbides have a catalytic activity similar to that of the platinum group metals [25-27]. High surface area materials, however, are generally needed for catalytic applications. Unfortunately, the preparation of high surface area carbides is very difficult. We have recently demonstrated a simple sonochemical synthesis of nanophase molybdenum carbide from the ultrasonic irradiation of molybdenum hexacarbonyl.

Sonochemical decomposition of molybdenum hexacarbonyl in hexadecane produced a black powder. X-ray powder diffraction (XRD) showed extremely broad peaks centered at a d

spacing of 2.4 Å, 1.5 Å, and 1.3 Å, which do not match body centered cubic (bcc) lines of molybdenum metal. After the heat treatment at 450°C under helium flow for 12 hours, sharper peaks in the XRD were observed at d spacing values of 2.39 Å, 1.49 Å, and 1.27 Å which match very well with face centered cubic (fcc) molybdenum carbide, Mo<sub>2</sub>C. Elemental analysis also confirmed the stoichiometry of 2Mo/C, but with some oxygen as discussed below. The formation of molybdenum carbide can be explained by the disproportionation of carbon monoxide on the active metal surface to form carbon and carbon dioxide [28].

The solid is an extremely porous aggregate of roughly 2 nm diameter clusters, as shown in the high resolution TEM (Figure 3). This is in good agreement with the 1.6 nm particle size calculated from the line broadening of X-ray powder diffraction. The surface area determined by BET gas adsorption isotherms was 188 m<sup>2</sup>/g.

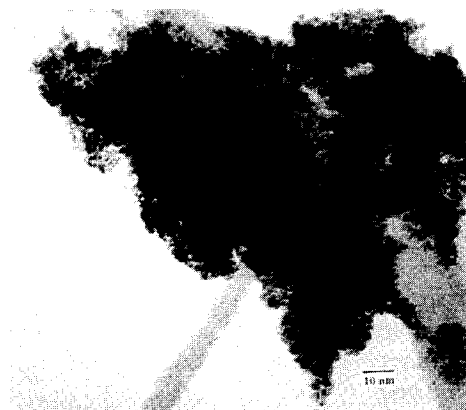


Figure 3. Transmission electron micrograph of sonochemically produced Mo<sub>2</sub>C, obtained on a Phillips CM-12 electron microscope.

Even after heat treatment at 450°C under helium, the sample still contained about 4 weight percent of oxygen. Since the presence of oxygen could poison the catalytic activity, it was removed before catalytic studies by heating in a flow of 1:1 CH<sub>4</sub>/H<sub>2</sub> 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 CH<sub>4</sub>/H<sub>2</sub> mixture was 27.5 cm<sup>3</sup> (STP)/min. After the heat treatment, the elemental analysis results showed the sample was pure Mo<sub>2</sub>C; oxygen, excess carbon, and hydrogen had been removed. Electron micrographs showed that the materials was still porous and was composed of particles of 3 nm in diameter. The BET surface area decreased slightly to 130 m<sup>2</sup>/g.

The catalytic activity of the sonochemically produced molybdenum carbide was tested for dehydrogenation of cyclohexane, as a function of temperature for samples pretreated under CH<sub>4</sub>/H<sub>2</sub> at 500°C for 48 hours. At all the reaction temperatures, benzene was the *only* product formed for either sample. No hydrogenolysis products were detected. Samples heat treated under helium (i.e., with oxide impurity) had the same selectivity (benzene is still the only product), but with somewhat lower activity. These results demonstrate that the sonochemically prepared molybdenum carbide is an excellent dehydrogenation catalyst and a rather poor hydrogenolysis catalyst. This is also confirmed by the complete lack of activity for ethane hydrogenolysis to methane.

The catalytic properties of Mo<sub>2</sub>C (fcc) and Mo<sub>2</sub>C (hcp) have been studied intensively in recent years [25-28]. CO hydrogenation, alkene hydrogenation, and hydrocarbon isomerization and hydrogenolysis have been investigated. In spite of the importance of the reaction, however, few reports mention Mo<sub>2</sub>C as an active catalyst for alkane dehydrogenation. As precedent for our studies, we note that carburization of Mo is known to temper Mo metal for dehydrogenation of hydrocarbons [29]. In contrast to our high selectivity against hydrogenolysis, Bell *et al.* have reported that there is some catalytic activity for ethane hydrogenolysis using conventional Mo<sub>2</sub>C(fcc) prepared by reduction and carburization of MoO<sub>3</sub> [25]. It seems the sonochemically prepared Mo<sub>2</sub>C (fcc) has different and more selective catalytic behavior than the molybdenum carbides generated by the other methods.

## CONCLUSIONS

A general sonochemical route to nanostructured materials has been developed for transition metals, alloys, and carbides. The sonochemical decomposition of volatile organometallic precursors in high boiling solvents produces nanostructured materials in various forms with high catalytic activities. We have prepared nanometer colloids, nanoporous high surface area aggregates, and nanostructured oxide-supported catalysts with this general route. Sonolysis of iron pentacarbonyl in the presence of silica, for example, gives us a supported amorphous nanostructured Fe/SiO<sub>2</sub> catalyst. The nanostructured Fe/SiO<sub>2</sub> catalyst showed higher catalytic activity for the Fischer-Tropsch synthesis compared to the conventional Fe/silica catalyst. High surface area alloys can also be prepared sonochemically by ultrasonic irradiation of solutions containing Fe(CO)<sub>5</sub> and Co(CO)<sub>3</sub>(NO) to make nanostructured Fe and Co metals or Fe-Co alloys. The sonochemically prepared Fe-Co alloys have large surface areas relative to bulk metal even after heat treatment. These Fe, Co, and Fe-Co powders show very high catalytic activity for the dehydrogenation and hydrogenolysis of cyclohexane, and surprisingly, the Fe-Co alloys are very selective for dehydrogenation. Finally, aggregates of nanometer-sized clusters of face centered cubic molybdenum carbide have been prepared sonochemically. The material is an extremely porous aggregate of  $\approx 2$  nm sized particles with a high surface area. The molybdenum carbide so produced is an active and highly selective dehydrogenation catalyst.

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## REFERENCES

- [1] G. Heinicke, *Tribochemistry* C. H. Verlag: Munich, 1984.
- [2] T. Tkacova, ed., *Proc. First Intl. Conf. Mechanochemistry: InCoMe '93, Košice, Slovakia* Cambridge Interscience: Cambridge, 1994
- [3] E. M. Gutman, *Mechanochemistry of Solid Surfaces*; World Scientific: Singapore, 1994.
- [4] K. S. Suslick, ed., *Ultrasound: Its Chemical, Physical, and Biological Effects* VCH Publishers: New York, 1988.
- [5] K. S. Suslick, *Science* **247**, 1439 (1990).
- [6] K. S. Suslick, *MRS Bulletin* **20**, 29 (1995).
- [7] K. S. Suslick, *Encyclopedia of Materials Science and Engineering*; R. W. Cahn, ed.; 3rd suppl., Pergamon Press: Oxford, 1993 p. 2093
- [8] K. S. Suslick, *Encyclopedia of Inorganic Chemistry*; R. B. King, ed.; J. Wiley & Sons: New York, 1994, vol. 7, pp. 3890-3905.
- [9] G. J. Price, ed., *Current Trends in Sonochemistry*; Roy. Soc. Chem.: London, 1992.
- [10] T. J. Mason, ed., *Advances in Sonochemistry*; JAI Press: London, 1990, 1991, 1993.
- [11] K. S. Suslick and D. J. Casadonte, *J. Amer. Chem. Soc.* **109**, 3459 (1987).
- [12] E. B. Flint and K. S. Suslick, *Science* **253**, 1397 (1991).
- [13] K. S. Suslick, R. E. Cline, Jr., and D. A. Hammerton, *J. Amer. Chem. Soc.* **106**, 5641 (1986).
- [14] K. S. Suslick, K. A. Kemper, *Bubble Dynamics and Interface Phenomena*; Blake J.R.; Thomas, N.; eds. Kluwer Publishers: Dordrecht, Netherlands, 1994, pp. 311-320.
- [15] K. S. Suslick, S. B. Choe, A. A. Cichowlas and M. W. Grinstaff, *Nature* **353**, 414 (1991).
- [16] M. W. Grinstaff, M. B. Salamon, and K. S. Suslick, *Phys. Rev. B* **48**, 269 (1993).
- [17] R. Bellissent, G. Galli, M. W. Grinstaff, P. Migliardo, and K. S. Suslick, *Phys. Rev. B* **48**, 15797 (1993).
- [18] M. W. Grinstaff, A. A. Cichowlas, S. B. Choe, and K. S. Suslick, *Ultrasonics* **30**, 168 (1992).
- [19] H. Weller, *Adv. Mater.* **5**, 88 (1993).
- [20] G. A. Ozin, *Adv. Mater.* **4**, 612 (1992).
- [21] K. E. Gonsalves, G. M. Chow, T. O. Xiao, R. C. Cammarata, eds. *Molecularly Designed Nanostructured Materials*, MRS Symp. Proc., vol. 351. Matls. Res. Soc.: Pittsburgh, 1994.
- [22] J. A. Dumesic, H. Topsøe, M. Boudart, *J. Catal.* **37**, 513 (1975).
- [23] T. Nishizawa and K. Ishida, *Bull. Alloy Phase Diagrams* **5**, 250 (1984).
- [24] M. Nakamura, B. J. Wood, P. Y. Hou, and H. Wise, *Proc. 4th Intl. Congress on Catal., Tokyo*, Kodansha Ltd., Tokyo, 1981, p. 432.
- [25] G. S. Ranhotra, G. W. Haddix, A. T. Bell and J. A. Reimer, *J. Catal.* **108**, 40 (1987).
- [26] J. S. Lee, S. T. Oyama and M. Boudart, *J. Catal.* **125**, 157 (1990).
- [27] M. J. Ledoux, C. Pham-Huu, J. Guille, and H. Dunlop, *J. Catal.* **134**, 383 (1992).
- [28] L. Volpe and M. Boudart, *J. Solid State Chem.* **59**, 332 (1985).
- [29] E. I. Ko and R. J. Madix, *Surf. Sci.* **100**, L449, L505 (1980).



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