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NANOSTRUCTURED
MATERIALS

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Nanostructured Materials

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PREFACE

Our ability to engineer novel structures at the molecular and supramolecular levels has led to unprecedented opportunities in materials design. It has fueled rapid development in nanotechnology for the past decade, leading to the creation of new materials with interesting nanometer-scale features. This volume presents the latest advances in this exciting interdisciplinary field, with contributions from chemical engineers, chemists, physicists, materials scientists, and bioengineers. It describes a "bottom-up" approach to designing nanostructured systems for a variety of chemical, physical, and biological applications.

Specifically, this volume focuses on the synthesis, processing, and structural tailoring of nanocrystalline and nanoporous materials. *Nanocrystalline materials* possess unique hybrid properties characteristic of neither the molecular nor the bulk solid-state limits and may be confined in nanometer-sized domains in one, two, or three dimensions for unusual size-dependent behavior. *Nanoporous materials,* characterized by well-defined pores or cavities in the nanometer size regime and controlled pore diameter and structure, give rise to unique molecular sieving capabilities and ultrahigh internal surface areas. Nanoporous structures also act as hosts and templates for the fabrication of quantum dots and quantum wires.

The chapters in this volume present detailed insights into the synthesis–structure–properties relationships of nanostructured materials. In particular, the catalytic and photocatalytic properties of nanoclusters and nanostructured materials with ultrahigh surface-to-volume ratio are demonstrated. The gas absorption characteristics and surface reactivity of nanoporous and nanocrystalline materials are shown for various separation and reaction processes. In addition, the structural manipulation, quantum confinement effects, transport properties, and modeling of nanocrystals and nanowires are described. The biological functionality and bioactivity of nanostructured ceramic implants are also discussed.

It is our hope that this volume illustrates the potential of nanostructured materials with multifunctionalities for a wide variety of applications. Chemical engineers, with their broad training in chemistry, processing, systems engineering, and product design, are uniquely positioned to play a pivotal role in this burgeoning field of nanotechnology. Active efforts in this research direction will impact how we tailor novel materials for areas such as catalysis and separations and how we integrate miniaturized systems such

as microreactors, fuel cells, sensors, and batteries. Research in this exciting frontier will also lead to new devices for optical, electronic, magnetic, thermoelectric, and biomedical applications.

This volume is dedicated to Professor James Wei on the occasion of his 70th birthday, for his leadership in *Advances in Chemical Engineering* and his vision for our profession.

JACKIE Y. YING
VOLUME EDITOR

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ENGINEERED SYNTHESIS OF NANOSTRUCTURED MATERIALS AND CATALYSTS

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The unusual structural and electronic properties of nanostructured materials, as they relate to recent observations of enhanced catalytic reactivities, are examined. The data suggest a need for advanced synthetic nanostructured materials processes producing high-purity crystallites in variable grain sizes in the range 1–20 nm. Within the past 5 years a wide variety of new processes have been discovered, and their capabilities are compared. One novel approach has been centered on adjusting the fluid dynamics of fast-flowing, liquid-slurry streams to conduct nanostructured materials synthesis within a cavitating bubble zone. The results of the synthesis method is to produce high shear and in situ calcination by shock wave heating and high Reynolds numbers. Nanostructured materials produced by hydrodynamic cavitation resulted in exceptionally high phase purity. In most cases, finished nanostructured metal oxides flowed directly from the processor, requiring little or no postsynthesis calcination. In many cases, the grain sizes of metal oxides and supported metals could be adjusted in the range 1–20 nm, and crystallographic strain could be systematically introduced in several classes of materials such as titania, CuO in Cu Zn Al O methanol synthesis catalysts, and piezoelectric materials. The method is inherently a high-volume, continuous process. © 2001 Academic Press.

I. Introduction

   Both the discovery of new synthesis processes for nanostructured materials and the demonstration of the highly reactive properties of these materials have increased rapidly within recent years. The new synthesis processes have made available nanostructured materials in a wide variety of compositions of metal oxides and metals supported on metal oxides, which have led to recognition of their exceptional chemical, physical, and electronic properties. The objective of this review is to provide recent results on synthesis of nanostructured materials using the novel processes that were developed in these laboratories recently and to contrast them to other important, new methods. Because some of the most important applications of nanostructured materials are as catalysts for chemical processing, several key reports on enhanced catalytic reactivity of nanostructured grains will be discussed along with the pertinent theory responsible for controlling both activity and selectivity of these new catalysts.

   Over the past 30 years, our laboratory has examined the synthesis of nanostructured materials for advanced catalysts. The first process for the synthesis of fine grains of cobalt molybdates for hydrodesulfurization catalysis

(Moser, 1977, 1978a) involved a supercritical fluid synthesis of a special form of alumina having all octahedral Al^{3+} on its surface. This permitted the facile growth of Co and Mo onto this surface to provide a bimetallic structure. Using similar techniques, this type of alumina was combined with a wide variety of rare earth metal ions for HDS catalysis (Moser, 1978b,c), in which the dispersion of the rare earth oxide over the nanostructured metal oxide support was high. The next catalyst synthesis process developed was the high-temperature aerosol decomposition (HTAD) process (Moser, 1991, 1993; Moser and Cnossen, 1992; Moser and Connolly, 1996; Moser et al., 1993, 1994, 1996a; Moser and Lennhoff, 1984, 1989) and was based on an early patent by Ebner (1939, 1951, 1953) used for the synthesis of simple metal oxides for ceramics applications. This process had the advantage of synthesizing nanostructured grains of simple and complex metal oxides but also resulted in high-phase purities of multimetallic perovskite, spinel, and scheelite materials. Furthermore, it resulted in metastable nonthermodynamic phases due to the fine crystallite grains in higher alcohol synthesis catalysts (Moser and Connolly, 1996) and maleic anhydride, V–P–O, catalysts (Michalakos et al., 1995; Moser, 1996). High-powered ultrasound was used in the synthesis (Emerson et al., 1998) of a wide variety of metal oxides and supported metal catalysts. The high-shear environment and shock wave heating provided by acoustically generated cavitation resulted in catalyst grains that were in all cases smaller than classically prepared materials, and the method resulted in Au–Pt alloys supported on titania in much higher alloy phase purity (Emerson et al., 1998) compared to classical synthesis. In recent years, we discovered that hydrodynamic cavitation generated by mechanical means (Moser, 1995a,b; Moser et al., 1995b, 1996b; Sunstrom et al., 1996) could be used to synthesize advanced catalysts, ceramics, and electronic materials in high-phase purities and as nanostructured grains. The most recent process discovered in our labs utilized a new device for the mechanical generation of cavitation (Moser et al., 1999), in which the bubble dynamics, shock wave, and shear could be controlled over an exceptionally wide range using equipment manufactured by Five Star Technologies and invented by Kozyuk (1996, 1998, 1999a–d, 2000a,b). This equipment offers the opportunity to use a range of engineering techniques and fluid dynamics phenomena to control the synthesis of nanostructured materials. This is the principal emphasis of this report and is described in Section IV.A.

II. Properties and Reactivities of Nanostructured Materials

An examination of recent information on the properties, structures, and reactivities of nanostructured materials indicates the importance of

discovering new synthetic procedures to fabricate such materials. Experimental data on the properties and catalytic reactivities of nanostructured materials reported within the past 5 to 10 years, coupled with theoretical computations in the older literature, demonstrate the significance of nanostructured materials having primary, crystallographic grain sizes in the range 1–20 nm. To put this discussion of novel synthetic techniques into perspective, a short review of the properties and reactivities of nanostructured materials will be given.

A. STRUCTURE AND ELECTRONIC PROPERTIES OF NANOSTRUCTURED MATERIALS

Although Baetzold's (1971, 1973) molecular orbital calculation performed nearly 30 years ago predicted that the ionization potential of nanostructured metals should increase as their grain sizes decrease, only recently has this been verified experimentally. Measurements on several metals having cluster sizes ranging from 2 to 140 atoms (de Heer, 1993) showed a systematic increase in the ionization potential for all metals studied as the cluster size decreased. The ionization potential of a 140-metal-atom cluster of Al increased from 4.7 to 6.5 eV for a 5-atom cluster. In our view this is an exceptionally important finding because it suggests that by systematically changing the grain size of a metal or supported metal through synthesis, one should be able to adjust the overlap integral between the donating metal electrons contained in nonbonding orbitals and the empty antibonding orbitals of a substrate so that an optimum energy relation exists for electron transfer and activation of either a catalytic or noncatalytic reaction. The basic theory for noncatalytic systems was described by Woodward and Hoffmann (1970), and the relationship of metallic band theory to reacting substrates was described by van Santen and Niemantsverdriet (1995). The data and reaction theory suggest that a key requirement of any nanostructured materials synthesis process is the capability to systematically vary the grain size of the crystallites between 1 and 20 nm without changing the chemistry by which the particles are produced. If this can be accomplished, the ionization potential of the different nano-sized grains can be adjusted for most catalytic reactions for optimum metal–substrate activation and maximized rates.

The high metal atom surface-to-volume ratio observed in nanostructured materials not only has importance to the number of active sites in a catalyst, but also can influence the oxygen and other anion-defect chemistry and the observation of metastable phases. Siegel's (1991, 1994) computations indicated that the percentage of metal atoms on the surface of a crystallite increased from a few percent in a 100-nm particle to about 90% in a

1-nm grain. The importance of this observation is that it predicts that surface free energy should dominate phase formation in nanometer grains of crystals rather than bulk thermodynamics. It predicts that metastable phases should be observed for many nanostructured materials. Our own aerosol synthesis (Moser and Connolly, 1996) of spinels resulted in the formation of nanostructured, metastable grains of a cubic spinel over the entire substitution series from $x = 0.0$ to 0.90, $Cu_xZn_{1-x}Cr_2O_4$, instead of the tetragonal phase. The synthesis of zirconia by hydrodynamic cavitation (Moser et al., 1995b) resulted in fine crystallites of cubic zirconia that transformed to the monoclinic phase upon heating. Furthermore, the aerosol synthesis (Moser and Cnossen, 1992) of both MoO_3 and Bi_2O_3 resulted in the formation of metastable β-MoO_3 and β-Bi_2O_3 as nanostructured grains, which transformed to their respective α-structures upon calcination and grain growth. This aspect of nanostructured catalyst synthesis offers the possibility for the formation of high-temperature stable, metastable compositions for application in high-temperature turbine combustion. The high surface atom–to-volume ratio of nanocrystalline ceria was suggested (Tschöpe et al., 1996) to be responsible for its high oxygen defect concentration and surface conductivity. This aspect is especially important to hydrocarbon partial oxidation catalysis because it affords the high oxygen mobility to balance the surface oxidation and reduction processes required for selective catalysis, but it also provides defect coordination sites for reacting molecules..

The change in grain size of a nanostructured catalyst results in the formation of cluster structures having stabilities that vary with grain size (Allpress and Sanders, 1970; Henry et al., 1997; Montejano-Carrizales and Moran-Lopez, 1992). The consequence of this variation is that the fraction of (111) and (100) crystallographic planes varies according to the fraction of icosahedron or truncated octahedral phases of supported metals. Naturally, these crystallographic planes show very different catalytic reactivities, depending on the reaction under consideration. A more important consequence of the decrease in grain size is the observation by van Hardveld and Hartog (1972) that as the crystallite size of a material decreases, the fraction of atoms in coordinatively unsaturated edge sites relative to atoms in the stable basal planes increases to dominate the atoms exposed to a reacting gas. Indeed, in propylene selective oxidation it was shown that as the crystallite size of MoO_3 was systematically decreased, exposing more of the (100) crystallographic edges, both the activity and the selectivity for forming acrolein increased (Volta et al., 1979; Volta and Tatibouet, 1985). However, for some catalytic processes, a small grain size can work to the detriment of selectivity. Okuhara and co-workers (1993) showed that exposing more of the edge sites of a V–P–O catalyst in the direct oxidation of butane to maleic anhydride resulted in a sharp decrease in selectivity.

B. Catalytic Properties of Nanostructured Materials

The preceding discussion points to a strong relationship between catalytic activity and selectivity that is controlled by grain-size effects. Although many studies, which are summarized later, have clearly demonstrated that turnover numbers (TON) greatly increase as the grain sizes decrease, the factors responsible for the observed rate acceleration have not been elucidated. The preceding discussion suggests that some of the controlling factors responsible for rate acceleration are (1) the increase in coordinatively unsaturated edge sites as grain sizes decrease, (2) the more favorable energy relationship between electrons on the metal or metal oxide surface and the antibonding orbitals of the substrate to be activated, (3) a higher concentration of anion vacancies and defect sites on the crystallite surface, (4) the higher electrical conductivity and ion mobility of nano-crystallite surfaces, (5) a higher degree of crystallographic strain as crystallites become smaller, and (6) alteration of the concentration of crystallographic planes of greatly differing activities as the catalyst crystallite size changes in the region 1–20 nm. In the following section, a few examples of a decrease in a catalyst's grain size leading to increased reactivity per metal atom center are given; however, there are some cases reporting that a decrease in the grain size resulted in a volcano plot, where reactivity decreased as the particle approached the 1- to 3-nm level. This phenomenon is expected if there is quantum mechanical control over the reactivity or when the particle becomes so small that it reacts with the support surface to generate a less reactive metal center.

The literature reports several cases where unusual catalytic properties resulted when nanostructured materials were compared to micrometer-size grains. When 1- to 5-nm particles of rhodium were synthesized on a polymer support (Busser *et al.*, 1996) and studied for their activity to hydrogenate cyclohexene, the turnover number smoothly increased by a factor of 10 as the particle size decreased from 5 to 1 nm. The synthesis of TiO_2 as nanometer grains by an aerosol process (Wold *et al.*, 1996) resulted in greatly enhanced activity as a photocatalyst for the decomposition of chlorocarbons. Thin films of TiO_2 were fabricated by spray pyrolysis techniques and were found to be especially active for chloro-organics photodecomposition. A sample of MoS_2 prepared with a high edge-to–basal plane ratio as 5- to 25-nm crystallites by an exfoliation technique led to a hydrodesulfurization activity that was four times greater than that of a large crystal of MoS_2 (Del Vallee *et al.*, 1994). Nanometer-size grains of supported iron and palladium catalysts (Wilcoxon *et al.*, 1993b) prepared by a micelle technique showed that pyrene was hydrogenated progressively faster up to two orders of magnitude in rate ratios when the particle sizes of palladium were systematically decreased from 14 to 3 nm. The preparation of gold particles in different grain sizes on titania

and iron oxide supports led to catalysts that were substantially more active (Haruta, 1997; Haruta *et al.*, 1993; Sanchez *et al.*, 1997; Tsubota *et al.*, 1994, 1995) and more stable for CO oxidation. The gold particles were found to be in a separate phase from the support and were a few nanometers in grain size. As the grain size was reduced from 8 nm to the 3-nm range, the reactivity increased dramatically. Other Au studies (Sze *et al.*, 1993) on CO oxidation on iron oxide of different morphologies showed that both grain size and the degree of roughness of the catalyst were important in controlling the CO oxidation activity. Grain sizes of 2–6 nm exhibited nearly twice the rate of 3- to 8-nm particles, and very uniform Au particles demonstrated a very low rate. In addition, the nonuniform Au particles deactivated at a much lower rate than uniform ones. Suslick and co-workers (Grinstaff *et al.*, 1992; Suslick *et al.*, 1994) reported the synthesis of nanometer grains of iron particles prepared by acoustic sonochemical means. These catalysts were prepared by sonolysis of $Fe(CO)_5$ in high surface areas as amorphous metallic particles due to the high heat-up and cooling rates inherent in the cavitation effect. They were much more effective than classically prepared materials in syngas conversion and hydrocarbon dehydrogenation.

Studies on the formation of metal clusters between 1 and 50 atoms by ion-bombardment techniques (Kaldor and Cox, 1990) led to several interesting phenomena as the number of atoms in the clusters decreased into the range 3–15 atoms. Deuterium adsorption studies showed that the H/M ratio greatly increased as the number of metal atoms per cluster decreased into the 10-atom range and greatly accelerated between 3 and 5 atoms for Rh, Pt, and Ni clusters. Similar preparations of Pt and Pd clusters were evaluated for their reactivity with methane (Cox *et al.*, 1990). Pt clusters showed a marked increase in reactivity below 8 atoms per cluster, whereas the Pd clusters exhibited a maxima between 10 and 15 atoms. Doesburg and co-workers (1987) synthesized copper supported on alumina-stabilized zinc oxide in grain sizes ranging from 3 to 20 nm. When these catalysts were evaluated for their methanol synthesis activity, a smooth increase in their turnover numbers resulted as the grain size decreased but showed a maxima at 4.5 nm. Smaller grain sizes resulted in much lower reactivities. Such a decline in activity for very small particles was observed in butane hydrogenolysis and hydrogen adsorption by nanostructured Pt supported on fine grains of titania (Salama *et al.*, 1993). The studies showed that the platinum was better dispersed as the titania grain size decreased, and the catalytic reactivity increased at lower Pt grain sizes down to 4 nm. Electron spin resonance studies showed that the reason for the reduction in activity for Pt below 4 nm was due to an SMSI surface reaction of Pt(0) with titania to form a partially oxidized Pt atom and formation of surface Ti^{3+}. Likewise, the hydrogenation of benzene by Rh supported on alumina (Fuentes and