Synthesis and Characterization of Chemically Tailored Monolithic Nanoporous Thin Films Using Molecular Beam Techniques

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◆ Approximately one-third of the material gross national product in the United States involves a catalytic process somewhere in the production chain. Understanding the synthesis and chemical activity of highly porous materials is a key step in achieving a fundamental scientific description of heterogeneous chemistry. ◆

We present the first synthesis and detailed characterization (structural and chemical) of nanoporous crystalline MgO, a catalytically relevant material, grown via reactive ballistic deposition. Due to the simple physical principles underlying the reactive ballistic deposition technique, we believe that it can be used for the growth of a broad range of chemically tailored, nanoporous materials with important applications in catalysis, chemical sensors, separations, and geochemistry.

The basic premise of ballistic deposition is that molecules incident from the gas phase stick at the first site they encounter at the surface of the solid without subsequent diffusion. Ballistic deposition at or near normal incidence results in relatively dense surfaces. At grazing incidence, the deposition cannot occur in regions behind high points on the surface due to simple shadowing and results in the formation of columnar, porous materials.

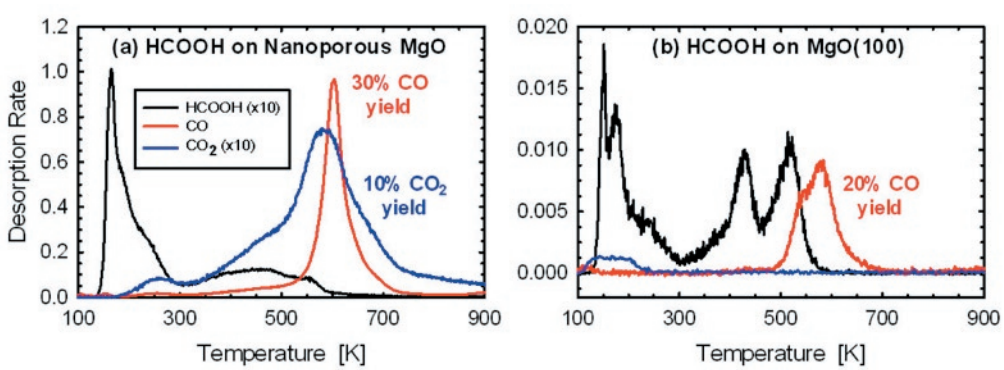
During FY 2001, we developed a novel reactive ballistic deposition technique for synthesis of highly porous MgO films. Using scanning and transmission electron microscopies, we demonstrated that the films deposited at oblique angles consist of an array of highly oriented, predominantly independent, columnar filaments tethered to the underlying substrate. Additionally, x-ray diffraction revealed that the nanoporous films are crystalline.

In FY 2002, we focused on the characterization of adsorption properties of nanoporous MgO films. Using physisorption of N_2, we determined the surface area and the distribution of binding sites on the surface where the relevant chemistry will occur. Films deposited at low temperatures and oblique angles of incidence exhibit extremely high surface areas of up to 1000 m^2/g. We also demonstrated that the nanoporous films have a greatly enhanced fraction of high-energy binding sites relative to the dense epitaxial film and are thermally stable up to ~900 kelvin.

Subsequently, the kinetics of uptake, sequestration, and release of a number of catalytically important gases such as NO_x, CH_4, O_2, H_2, CO_2, and H_2O by these porous materials were examined. In all cases, the adsorbates preferentially migrated to and occupied the most stable binding sites throughout the film, thereby demonstrating facile transport of reagents within the film. Co-adsorption studies demonstrated dynamic exchange of reagents between adsorption sites but did not yield measurable quantities of reaction products.

As a first step toward studying reactive chemistry relevant to catalysis, we began in FY 2003 to explore the reactivity of formic acid on these films. Formic acid can decompose via two channels, forming either CO and H_2O, or CO_2 and H_2. The desorption spectra from HCOOH on monocrystalline and nanoporous MgO are shown in the figure. On both surfaces, we observed that a certain fraction of HCOOH desorbed intact. On MgO(100), the HCOOH dissociation leads only to formation of CO and H_2O. In contrast, on nanoporous MgO, formation of CO_2 and H_2 is also observed. The presence of a new reaction channel is attributed to the high concentration of high-energy binding sites present on a nanoporous surface, in accord with N_2 physisorption measurement.

In collaboration with C. Campbell's group from the University of Washington, we also studied the dissociation of CH_4 on Pd nanoparticles supported on MgO(100). These experiments have been conducted for several Pd coverages and CH_4 beam energies. The resulting surface carbon was reacted with an O_2 beam to determine the CH_4 dissociation rate. We also examined the formation of CO_2 from CO and O_2 on these nanoparticles. The preliminary data indicate that both the CH_4 dissociation and CO oxidation reactions are enhanced on Pd nanoparticles.



Desorption products from HCOOH adsorbed on (a) nanoporous MgO and (b) monocrystalline MgO.